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GROWTH OF INP BASED FILMS USING THE HYDRIDE GROWTH TECHNIQUE.(U)
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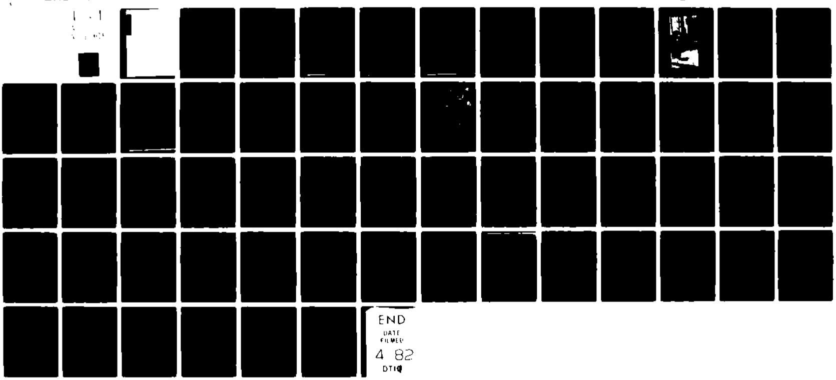

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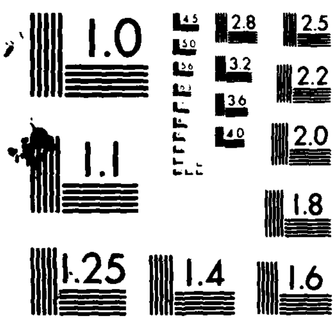
1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

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Growth of InP Based Films Using the Hydride Growth Technique

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ABSTRACT

A hydride growth system has been constructed that is capable of growing InGaAsP films or any ternary or binary combination. The system was designed to keep the background carrier density to a minimum as there are a number of device applications for low carrier concentration films. This was done by building a system that is leak tight down to 10^{-6}-cm^{-3}, and constructing a forechamber from which the substrate can be magnetically loaded through a gate valve. Therefore, the growth zone is never opened to the atmosphere during a growth run.

Thus far only InP films have been grown, but we plan to soon grow InGaAs films. The first films that were grown contained many hillocks, but their density was reduced in the later films by reducing the input HCl concentration. The HCl concentration in the deposition zone was increased by introducing HCl downstream from the liquid indium. This was done to try to reduce the silicon contamination. However, we found that this greatly reduced the growth rate, and in some instances the substrate was actually etched. This also occurred when the input HCl was not forced to come into intimate contact with the liquid indium. We, therefore, concluded that there was too much HCl in the deposition zone which impeded the deposition process.

Theoretical thermodynamic calculations were made on the effects of varying the deposition temperature, input HCl and PH_3 partial pressures, and downstream HCl partial pressure, as well as the dependence of the

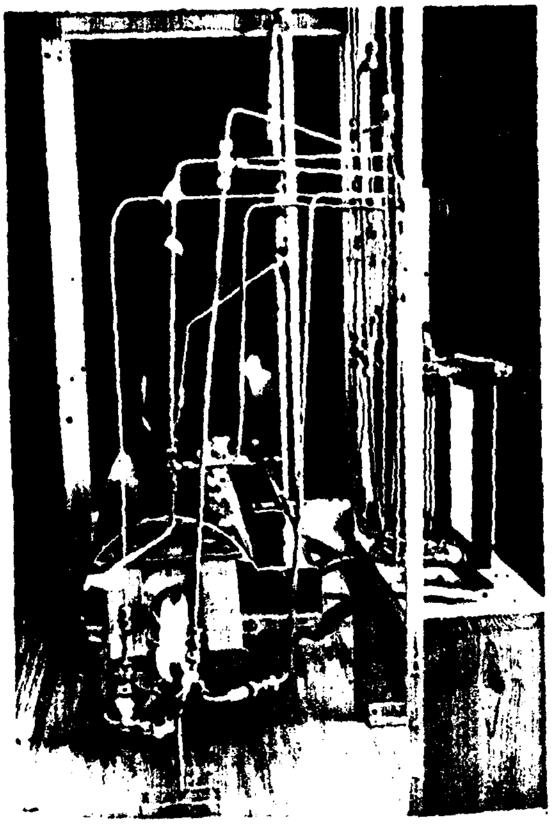
silicon activity on the HCl concentration and temperature. It was found that the most effective way to increase the deposition zone HCl concentration is to increase the input partial pressure since the HCl-In reaction is 99% efficient over a large range of temperatures and pressures. Increasing the deposition zone HCl concentration by introducing HCl downstream is not an effective method due to the fact that this impedes the deposition process. Increasing the PH_3 concentration is not as effective since it does not have as large an effect on the free energy change of the deposition reaction as does the HCl concentration. It is also shown that the silicon activity can be substantially reduced by increasing the deposition zone HCl concentration and lowering the deposition temperature.

I. GROWTH SYSTEM

A. Initial Design

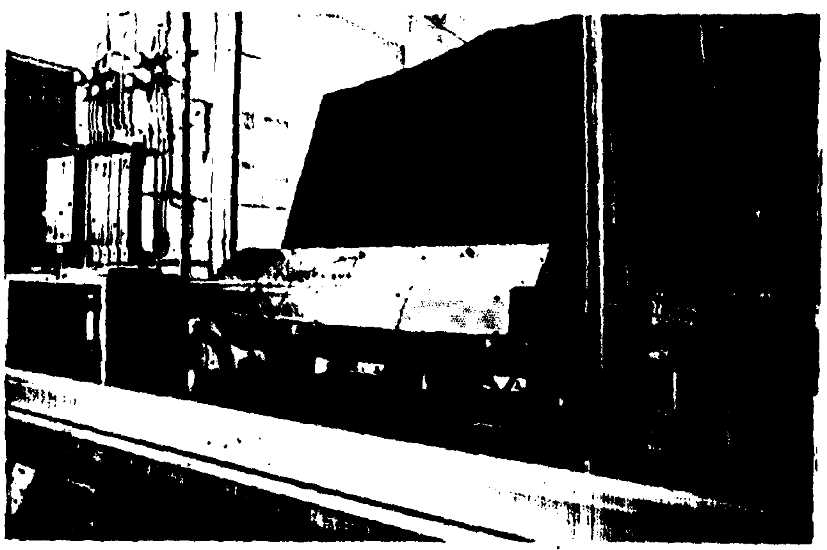
The first step in this project was to design and build a hydride growth system. Photographs of the system, which is a hybrid of the systems designed by Olsen[1] and by Johnston and Strege,[2] are shown in Figure 1 and a schematic of the system is shown in Figure 2. The toxic gases are contained in a vented enclosure, and the gases flow from the tanks through two stage regulators and one quarter or one eighth inch stainless steel tubing to rotameters where their calibrated flow rate is controlled by a needle valve. Rotameters were used both because they are much cheaper than mass flow controllers, and they do not need to be recalibrated constantly. The shut off valves used are Nupro bellows seal valves and the hydrogen gas used is purified using a Matheson hydrogen purifier.

The growth chamber shown in Figure 3 contains five zones - the forechamber, the predeposition, deposition, mixing, and source zones. A forechamber is used so that the substrate can be injected into the growth zone without fear of introducing outside contaminants. It is connected to the growth zone by a gate valve. The specimen is placed on the holder, the forechamber is closed, the gate valve is closed, the forechamber is evaculated, and then it is backfilled with hydrogen. After the furnace has reached the steady state profile, the specimen is moved into the predeposition position where it is bathed in PH_3. It is next placed in the growth position, and then it is retracted into the forechamber after the deposition process has been completed where it is allowed to cool.



(a)

(c)



(b)

Fig. 1. Photographs of the growth system (a) end view of the furnace, (b) side view of the furnace, and (c) vented enclosure containing some of the gases.

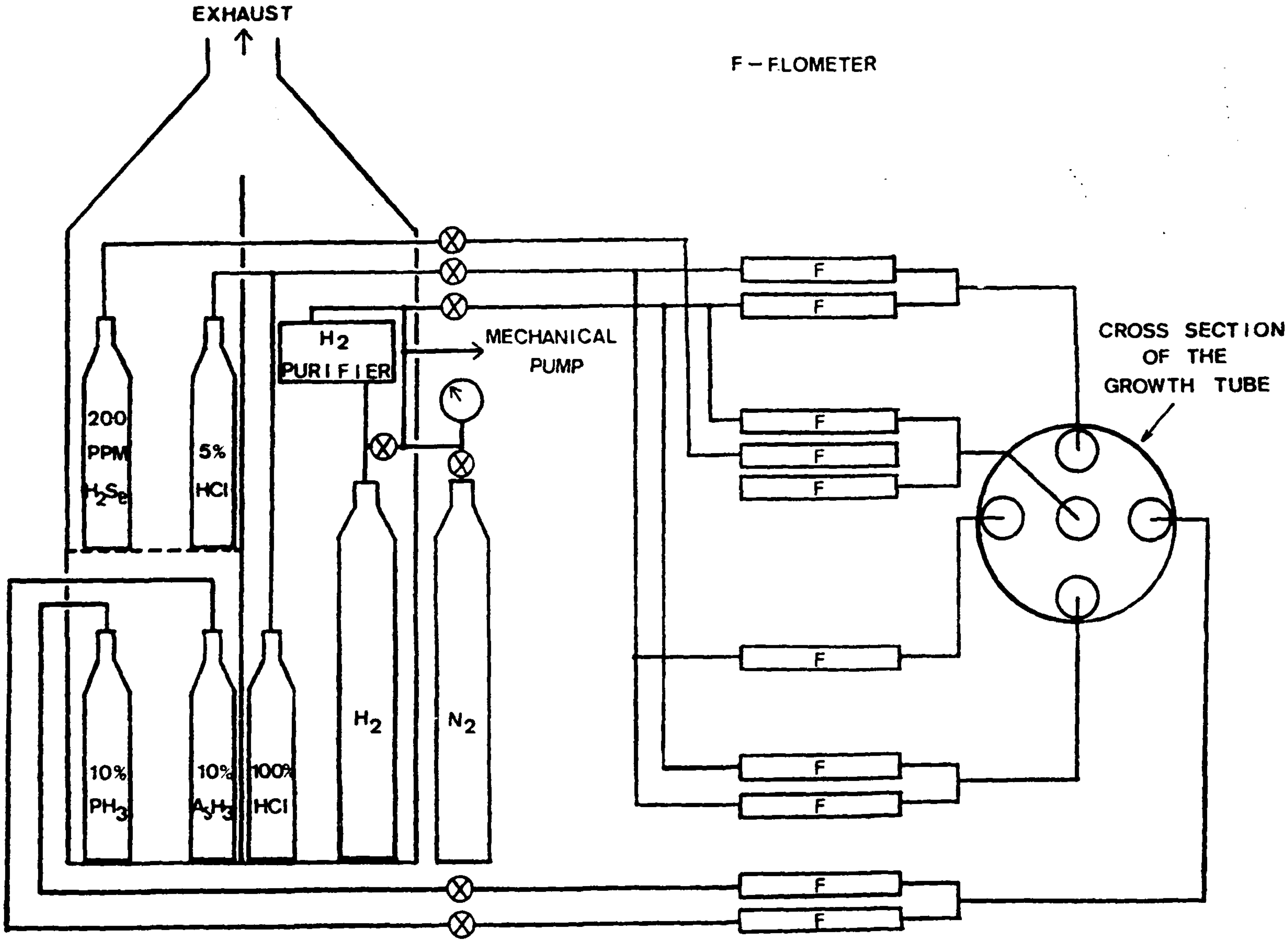


Fig. 2. Schematic diagram of the gas handling system.

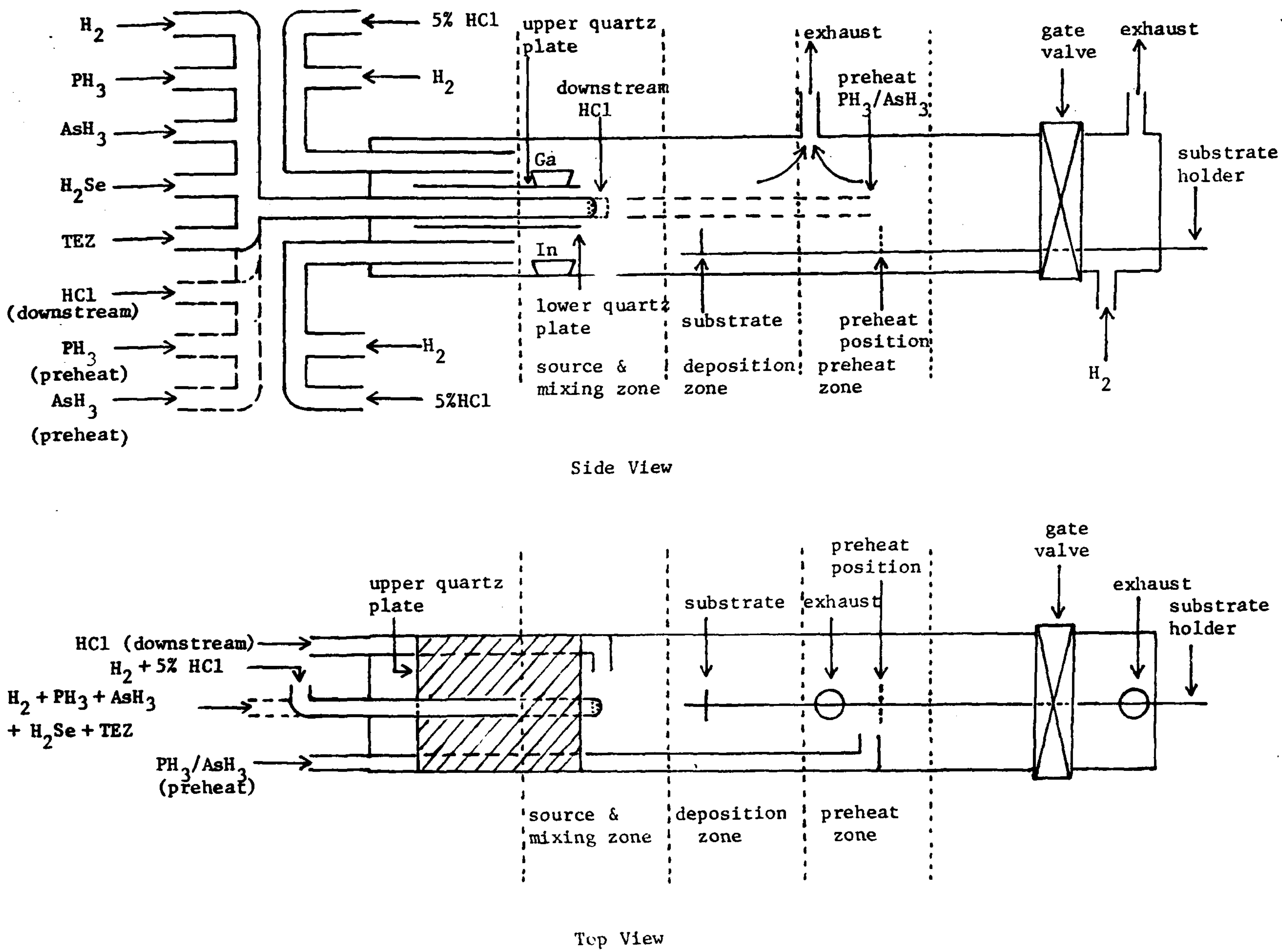


Fig. 3. A schematic of the growth tube.

The growth tube was designed for the growth of the quaternary, InGaAsP, and any ternary or binary combinations thereof. The cation compartments are separated so there is no mixing in the vicinity of the metal containing boats. The anion hydrides are injected downstream through a closed tube containing many small holes to facilitate the mixing process. Additionally, the system is designed so that HCl can be injected downstream in addition to flowing over the metal melts. The downstream HCl can be used to etch the substrate prior to deposition as well as impede the deposition on the walls of the growth tube. The boats are designed so that the HCl comes in intimate contact with the liquid metals to insure that the metal chloride reaction is driven to completion.

The gases in the cylinders in the vented enclosure shown in Figure 2 are 10% PH_3 in H_2, 10% AsH_3 in H_2, 200 ppm H_2Se in H_2, and 100% HCl (used to clean the system). The liquid diethyl zinc (DEZ) through which hydrogen is bubbled and the 5% HCl in H_2 used in the growth process are contained in cylinders inside of the growth vented enclosure. The exhaust gases are bubbled through silicone oil, burned, and then exhausted to the roof.

B. Design Changes

It has been found that it is difficult to completely retract the specimen into the forechamber because material is deposited from the vapor on to the push rod. Further, there is some concern about a small amount of leakage through the ultratorr fitting when it is loosened in order to move the push rod. Also, the pushrod might have impurities such as water apor adsorbed onto the rod. Therefore, the forechamber has been increased in size to make retraction of the push rod easier and

a magnetic loader has been built to eliminate the problem associated with the ultratorr fitting. A schematic of this loader is shown in Figure 4.

We also found that the exhaust tube would become clogged with precipitates from the vapor. Therefore, a mercury manometer was attached to the growth zone to monitor any pressure build ups, and the exhaust tube was moved to the cooler end beyond the region where most of the wall deposition occurred.

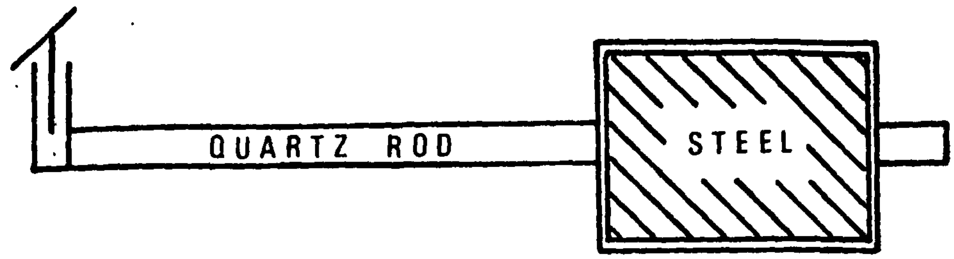
There is some concern that the purity of the HCl gas is not as pure as the PCl_3 vapor used in the chloride process.[3-5] In order to eliminate this variable, we are in the process of constructing a PCl_3 cracking furnace, which is shown in Figure 5. The PCl_3 is heated in hydrogen to such a temperature and pressure that the PCl_3 decomposes into HCl and primarly P_2 and P_4 although some PH_3 will be present. The outlet gas is passed through an ice water cold trap to precipitate out as much of the phosphorous containing compounds as possible.

The PCl_3 can bypass the cracking furnace so that films can be grown using the chloride method. Thus a useful comparison between the hydride and chloride[6-10] methods can be made.

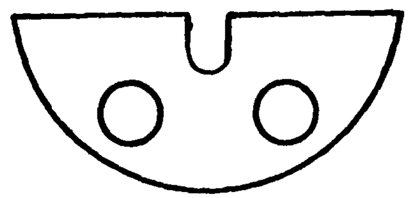
The system will also be constructed with an AsH_3 bubbler so that AsH_3 can be used instead of PH_3.

C. Film Growth

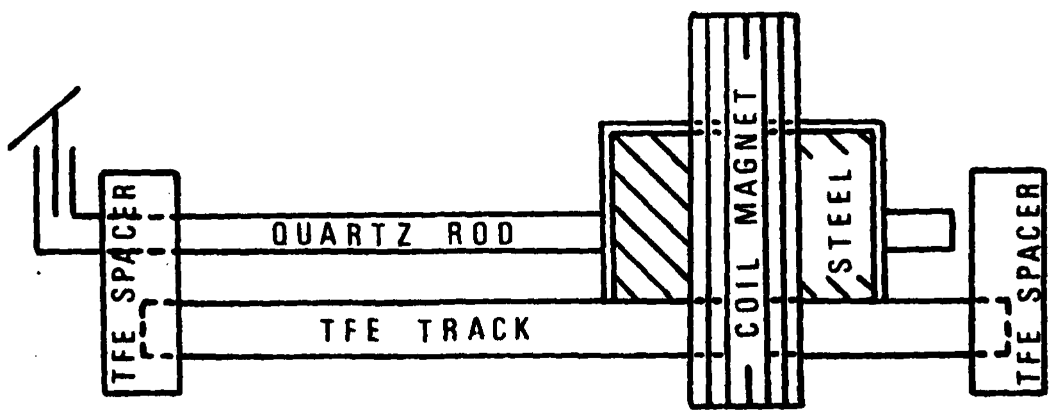
Homoepitaxial InP films were grown in the following manner. The furnace was turned on and allowed one hour to reach its steady state. The indium boat was in a thermal plateau of 800°C and the growth position for the substrate was at the end of a 650°C plateau. The gradient between these two constant temperature regions was about 6°C per cm. (See Figure 6).



The magnetically driven substrate pushing rod.



The teflon spacer.



The magnetically driven substrate moving system.

Figure 4. Schematic of the magnetic loader.

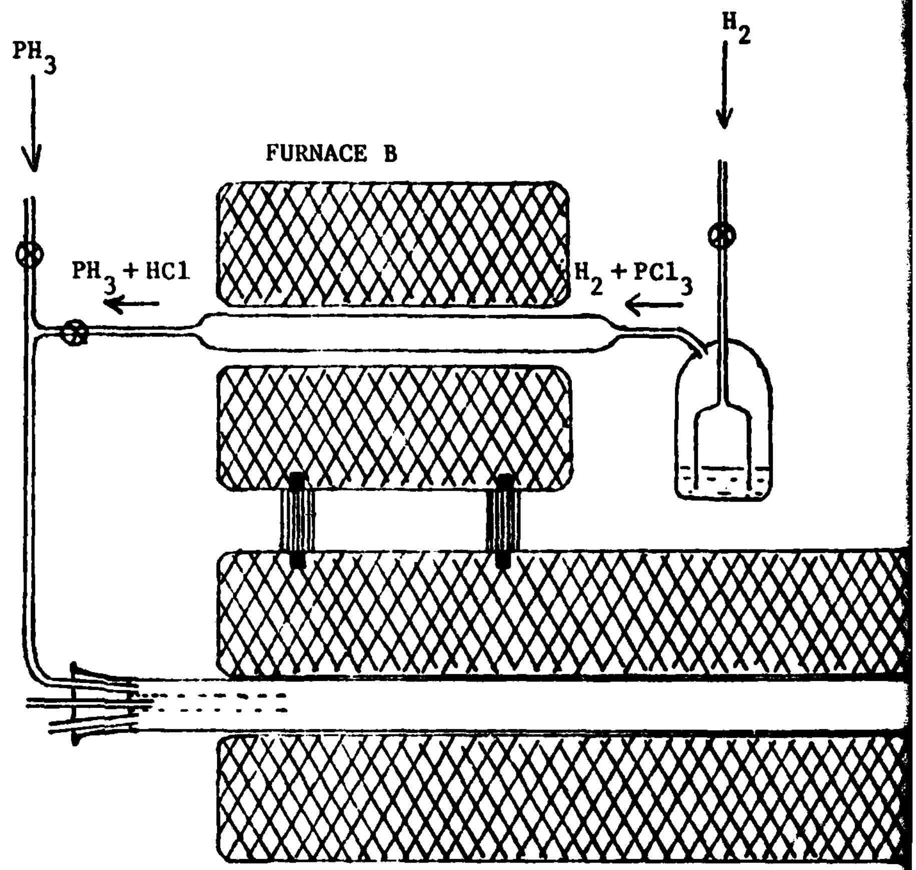
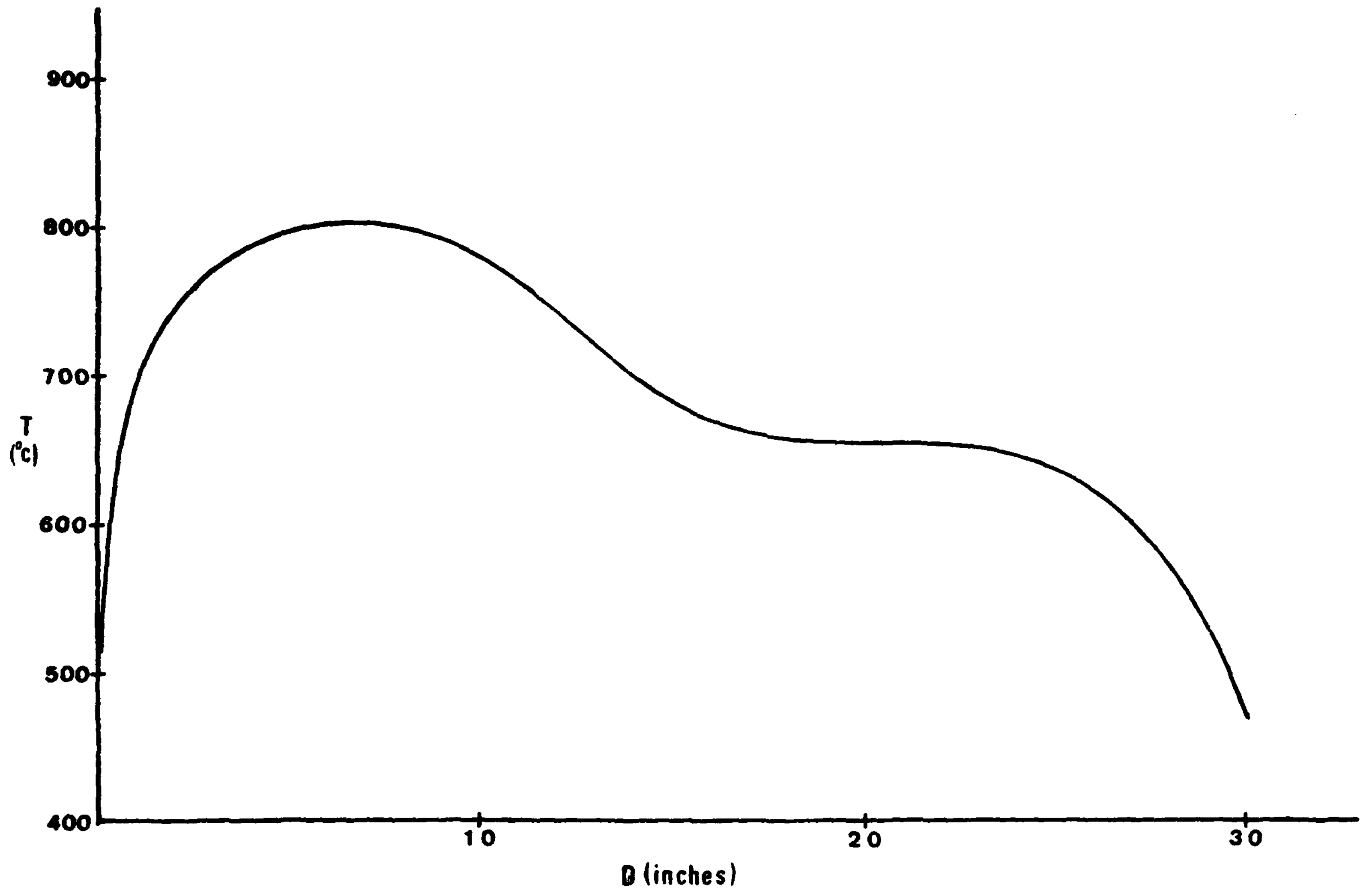


Figure 5. Schematic of the cracking furnace for the anion chlorides.


T
(°C)
900
800
700
600
500
400
10
20
30
D (inches)

Before the (001) insulating substrate oriented 3° toward the [110] direction (Crystal Comm) was placed in the substrate holder, it was polished in a manner similar to that described by Clawson et al.[11] This included a chemical-mechanical polish in a 1% bromine-methanol solution and a thorough wash in deionized water. Immediately before the substrate was mounted, it was soaked in concentrated KOH solution to remove the surface oxide, and was then rinsed in a 1% Br-Me solution. The substrate was placed in the forechamber, the forechamber was evacuated, and then it was back filled with hydrogen. Next, the gate valve was opened and the substrate was inserted into the predeposition position which was at the same temperature as the growth position - 650°C. It was held there for ten minutes being bathed in a 10% PH_3 in H_2 gas mixture flowing at 50-75 ccm, and then it was placed in the growth position. The predeposition PH_3 was turned off and the substrate was inserted into the growth position. The flow rate for the 10% PH_3 in H_2 was 50-75 ccm, the flow rate for the 5% HCl in H_2 was 100-150 ccm, and there was an additional flow of H_2 mixed in with the HCl gas mixture for a total flow rate of 500 ccm. These flow rates translate into the input partial pressures, $P_{HCl^o} = 10^{-2} - 1.5 \times 10^{-2}$ atm. and $P_{PH_3^o} = 10^{-2} - 1.5 \times 10^{-2}$ atm., which are similar to those used by Zinkiewicz et al.[2] The source and deposition temperatures are also similar. The film was deposited for a period of 30 minutes and then it was retracted to a position near the gate valve. It could not be retracted all the way into the forechamber because the substrate rod became coated with materials from the gas phase.

The primary focus was to examine how the input HCl, HCl^o, and input, PH_3, PH_3^o, flow rates affect the morphology. Our goal was to find the maximum

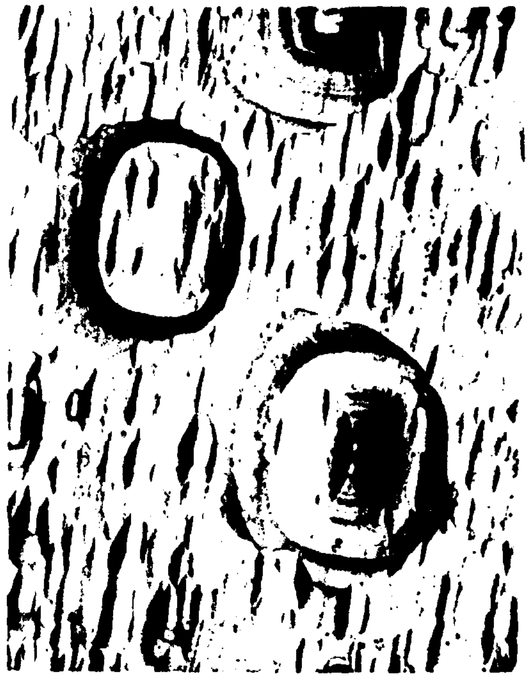
HCl^o/PH_3^o ratio for which a smooth film could be grown. We want to maximize this ratio because Zinkiewiez et al.[12] found that this minimizes the degree of compensation. Our preliminary results support this finding.

The photograph of the morphology shown in figure 7a is typical of a film grown with an HCl^o partial pressure of 1.5×10^{-2} atm. and a PH_3^o partial pressure of 1.0×10^{-2} atm. There it is seen that there are hillocks on top of the hillocks. The photograph in figure 1b is a typical morphology when equal partial pressures of 1.5×10^{-2} atm. were employed. The facets are more distinct and the surface is smoother, but it is still unacceptably rough. The morphology in figure 1c is for equal partial pressures of 1.0×10^{-2} atm. The hillocks are still present but their density is much reduced. These preliminary results suggest that the morphology depends on the magnitudes of the two partial pressures as well as their ratios.[12,13] At these partial pressures the total H_2 flow rate no doubt also affects the morphology. We will examine this effect in a later report.

A possible explanation of these observations is that hillocks form by growth around indium droplets which form when the indium is not given sufficient time to diffuse to its equilibrium position.[4] Thus, the morphology of the film grown with the HCl^o and PH_3^o pressures of .01 atm. is better than that grown with the HCl^o and PH_3^o pressures of .015 atm. because the rate of arrival of the indium atoms is less. This allows the surface indium atoms more time to diffuse to their equilibrium position before the next 'layer' of indium atoms arrive.

A possible explanation of the observation that there is less compensation in the films containing more hillocks is that more of the excess indium is tied up in the electrically inactive droplets. This assumes, of course, that some of the compensation is due to the excess indium.

7a



7b

7c

Figure 7. Micrographs of the hillocks formed on films for which the HCl^o and PH_3^o partial pressures were a) .01 and .015 atm., b) .015 and .015 atm., and c) .01 and .01 atm.

We also attempted to increase the deposition zone HCl concentration by introducing HCl downstream.[15] We found that doing this greatly impeded growth, and when the downstream HCl concentration was too high, etching of the substrate occurred. We observed similar behavior when the input HCl was not brought into intimate contact with the liquid indium in the source zone. Our conclusion, therefore, is that an increased deposition zone HCl concentration, whether the HCl comes from unreacted HCl in the source zone or HCl injected downstream, greatly inhibits the deposition process.

II. THEORETICAL STUDIES

While the furnace was being built and tested, theoretical studies of the growth processes were undertaken to better understand what the important growth paramters are. The studies continued after we had begun to grow films in order to better understand our results. These studies focused on the thermodynamic properties, and they include the concentration of HCl and InCl in the source zone in equilibrium with the liquid indium, the equilibrium concentration of PCl_3 under normal growth conditions, the effect of varying the deposition temperature, the effect of varying the input HCl and PH_3 pressures, and the effect of introducing HCl downstream. The silicon activity in the growth zone was also calculated as a function of the equilibrium HCl concentration.

A. Equilibrium Pressures of HCl and InCl in the Source Zone

In the source zone HCl reacts with the liquid indium according to the equation

$$HCl + In(l) \rightarrow InCl + \frac{1}{2} H_2 \qquad (1)$$

The equilibrium constant for the reaction is given by

$$\ln K_1 = \ln \left(\frac{P_{InCl}\, P_{H_2}^{1/2}}{P_{HCl}}\right) = -\frac{\Delta G_1}{RT} \qquad (2)$$

The input HCl pressure is HCl^o, so that the equilibrium InCl pressure is

$$P_{InCl} = HCl^o - P_{HCl} \quad . \qquad (3)$$

Because the total pressure is 1 atm.

$$P_{H_2} = 1 - P_{HCl} - P_{InCl} = 1 - P_{HCl^o} \qquad (4)$$

Substituting (3) and (4) into (2) yields

$$P_{HCl} = \frac{P_{HCl^o}\,(1 - P_{HCl^o})^{1/2}}{\exp(-\Delta G_1/RT) + (1 - P_{HCl^o})^{1/2}} \qquad (5)$$

ΔG_1 can be found from the equations

$$\Delta G_1 = \Delta G_o \frac{T}{T_o} + \Delta H_I - aT\ln T - \frac{1}{2}\Delta b\, T^2 - \frac{1}{2}\Delta c/T - IT \qquad (6)$$

where

$$\Delta H_I = \Delta H_o - \Delta a T_o - \frac{1}{2}\Delta b\, T_o^2 + \Delta c/T_o \qquad (7)$$

and

$$I = \frac{\Delta H_I}{T_o} - \Delta a \ln T_o - \frac{1}{2}\Delta b T_o - \frac{1}{2}\Delta c/T_o^{\,2} \qquad (8)$$

Using the thermodynamic values listed in Table 1,

$$\Delta G_1 = 4122 + 1.06\, T\ln T + .5075\, T^2 \times 10^{-3} + 1.19 \times 10^5/T - 20.795T \qquad (9)$$

Table 1. The standard enthalpies and entropies and the heat capacity coefficients for the phosphorous and indium compounds involved in the transport process (from Shaw[16]).

Specie (gaseous unless designated)	$\Delta H^\circ_{f.298}$ (kcal mol^{-1}	S°_{298} (e.u)	$C^\circ_p = a + b\,T + CT^{-2}$ (e.u.)		
			a	b x 10^3	c x 10^{-5}
P_2	42.68	52.11	8.46	0.41	-0.84
P_4	30.77	66.89	19.31	0.42	-3.04
PH_3	5.47	50.24	8.56	6.85	-1.68
PCl_3	-61.03	74.42	19.54	0.25	-2.15
InCl	-16.7	59.3	8.93	--	-2.09
$InCl_3$	-90.0	82.3	18.00	1.70	--
In(1)	0.8	15.53	7.10	--	--
In	57.0	41.51	4.55	1.77	-0.16
InP(s)	-14.6	14.28	12.27	--	-1.14
HCℓ	-22.06	44.64	6.18	1.34	.35
H_2	0	31.21	6.58	.65	.12
$C\ell_2$	0	53.29	8.76	.26	-.65

In Table 2 the HCl, InCl, and H_2 concentrations, as well as the fraction of the input HCl(HCl^o) converted to InCl (FC) and the molar free energy change, GO, for the reaction (1) are tabulated as a function of source temperature, T_s, and input HCl pressure. It is clear from this table that >98.7% of the HCl is converted to InCl at all temperatures considered. Thus, from a thermodynamic point of view, as opposed to a kinetic point of view, there is no need for the source temperature to be high. This could be an important point because the silicon activity is greater at higher temperatures.[17]

Table 2. The reaction temperature, T_s, molar free energy change, GO, equilibrium HCl, InCl, and H_2 partial pressures, fraction of input HCl converted to InCl, FC, for different input HCl pressures, HCl^o.

T	GO	HCl^o	HCL	INCL	H2	FC
700.	-8412.					
		.100E-02	.127E-04	.987E-03	.9990	.9873
		.178E-02	.226E-04	.176E-02	.9982	.9873
		.316E-02	.402E-04	.312E-02	.9968	.9873
		.562E-02	.714E-04	.555E-02	.9944	.9873
		.100E-01	.127E-03	.987E-02	.9900	.9873
		.178E-01	.224E-03	.176E-01	.9822	.9874
		.316E-01	.396E-03	.312E-01	.9684	.9875
		.562E-01	.696E-03	.555E-01	.9438	.9876
		.100E+00	.121E-02	.988E-01	.9000	.9879
750.	-8989.					
		.100E-02	.119E-04	.988E-03	.9990	.9881
		.178E-02	.211E-04	.176E-02	.9982	.9881
		.316E-02	.375E-04	.312E-02	.9968	.9881
		.562E-02	.666E-04	.556E-02	.9944	.9882
		.100E-01	.118E-03	.988E-02	.9900	.9882
		.178E-01	.209E-03	.176E-01	.9822	.9882
		.316E-01	.370E-03	.313E-01	.9684	.9883
		.562E-01	.649E-03	.556E-01	.9438	.9885
		.100E+00	.113E-02	.989E-01	.9000	.9887
800.	-9559.					
		.100E-02	.112E-04	.989E-03	.9990	.9888
		.178E-02	.199E-04	.176E-02	.9982	[illegible]
		.316E-02	.353E-04	.313E-02	.9968	.9888
		.562E-02	.627E-04	.556E-02	.9944	.9889
		.100E-01	.111E-03	.989E-02	.9900	.9889
		.178E-01	.197E-03	.176E-01	.9822	.9889
		.316E-01	.348E-03	.313E-01	.9684	.9890
		.562E-01	.611E-03	.556E-01	.9438	.9891
		.100E+00	.106E-02	.989E-01	.9000	.9894
850.	-10124.					
		.100E-02	.106E-04	.989E-03	.9990	.9894
		.178E-02	.188E-04	.176E-02	.9982	.9894
		.316E-02	.335E-04	.313E-02	.9968	.9894
		.562E-02	.594E-04	.556E-02	.9944	.9894
		.100E-01	.105E-03	.989E-02	.9900	.9895
		.178E-01	.187E-03	.176E-01	.9822	.9895
		.316E-01	.330E-03	.313E-01	.9684	.9896
		.562E-01	.579E-03	.557E-01	.9438	.9897
		.100E+00	.101E-02	.990E-01	.9000	.9899

Table 2 - Continued.

900.	-10683.					
		.100E-02	.101E-04	.990E-03	.9990	.9899
		.178E-02	.180E-04	.176E-02	.9982	.9899
		.316E-02	.319E-04	.313E-02	.9968	.9899
		.562E-02	.567E-04	.557E-02	.9944	.9899
		.100E-01	.101E-03	.990E-02	.9900	.9899
		.178E-01	.178E-03	.176E-01	.9822	.9900
		.316E-01	.315E-03	.313E-01	.9684	.9900
		.562E-01	.553E-03	.557E-01	.9438	.9902
		.100E+00	.960E-03	.990E-01	.9000	.9904
950.	-11238.					
		.100E-02	[illegible]	[illegible]	.9990	.9903
		.178E-02	[illegible]	[illegible]	[illegible]	.9903
		.316E-02	[illegible]	[illegible]	.9968	.9903
		.562E-02	[illegible]	[illegible]	.9944	[illegible]
		.100E-01	[illegible]	[illegible]	[illegible]	[illegible]
		.178E-01	[illegible]	[illegible]	[illegible]	[illegible]
		.316E-01	[illegible]	[illegible]	.9681	[illegible]
		.562E-01	[illegible]	[illegible]	.9438	.9906
		.100E+00	[illegible]	[illegible]	.9000	[illegible]
1000.	-11787.					
		.100E-02	[illegible]	[illegible]	[illegible]	[illegible]
		.178E-02	[illegible]	[illegible]	[illegible]	[illegible]
		.316E-02	.296E-04	[illegible]	[illegible]	[illegible]
		.562E-02	.526E-04	[illegible]	.9944	[illegible]
		.100E-01	.934E-04	[illegible]	.9900	[illegible]
		.178E-01	[illegible]	.176E-01	.9822	[illegible]
		.316E-01	.292E-03	[illegible]	.9684	[illegible]
		.562E-01	.513E-03	[illegible]	.9438	[illegible]
		.100E+00	.890E-03	.991E-01	.9000	[illegible]

B. Equilibrium PCl_3 Concentration

In a number of computations such as those by Shaw,[16] it is assumed that the primary constituents are H_2, InCl, HCl, P_4, P_2 and PH_3. We wanted to verify that the equilibrium PCl_3 concentration is substantially less than those of the other gases both because it could affect the calculations for the other gases and we will later want to make a comparison between the hydride and chloride techniques.

For the reactions

$$PCl_3 + \frac{3}{2}(1+y)\ H_2 \rightarrow (1-y)\ \frac{x}{2}\ P_2 + (1-y)(\frac{1-x}{4})\ P_4 + yPH_3 + 3HCl \qquad (10)$$

$$P_2 \rightarrow \frac{1}{2}\ P_4 \qquad (11)$$

$$PH_3 \rightarrow \frac{x}{2}\ P_2 + (\frac{1-x}{4})\ P_4 + \frac{3}{2}\ H_2 \qquad (12)$$

one can calculate the free energy change, ΔG, and the equilibrium constant, K, for these reactions using the thermochemical data compiled by Shaw[16] and listed in Table 1. First a value of P_{P_4} is assumed and is used to compute P_{P_2} with the equation

$$P_{P_2} = P_{P_4}^{1/2}/K_3 \qquad (13)$$

For the conservation of phosphorous

$$P_{PCl_3^o} - P_{PCl_3} = 2P_{P_2} + 4P_{P_4} + P_{PH_3} \qquad (14a)$$

where $P_{PCl_3^o}$ is the input PCl_3 partial pressure.

Assuming P_{PCl_3} is negligible

$$P_{PH_3} \simeq P_{PCl_3^o} - 2P_{P_2} - 4P_{P_4} \qquad (14b)$$

From the conservation of chlorine

$$P_{HCl} = 3(P_{PCl_3^o} - P_{PCl_3}) \simeq 3P_{PCl_3} \tag{15}$$

and the fact that the total pressure is 1 atm.

$$P_{H_2} \simeq 1 - P_{P_2} - P_{P_4} - P_{HCl} - P_{PH_3} . \tag{16}$$

Now, knowing that

$$x = \frac{P_{P_2}}{P_{P_2} + 2P_{P_4}} \tag{17}$$

the equilibrium constant

$$K_4 = \frac{P_{P_2}^{\ x/2}\ P_{P_4}^{\ 1-x/4}\ P_{H_2}^{\ 3/2}}{P_{PH_3}} \tag{18}$$

can be computed and compared with the value of K_4 determined from ΔG_{12}. A new guess is made for the value of P_{P_4} and the process is repeated until the two computed values of K_4 are the same. The value of y in Eq. (10) is given by

$$y = \frac{P_{PH_3}}{xP_{P_2} + (1-x)P_{P_4} + P_{PH_3}} \tag{19}$$

and is used to calculate the thermodynamic parameters in the set of equations, 6-8.

Finally,

$$P_{PCl_3} = \frac{P_{P_2}^{\ (1-y)x/2}\ P_{P_4}^{\ (1-y)(1-x)/4}\ P_{PH_3}^{\ y}\ P_{HCl}^{3}}{K_2\ P_{H_2}^{\ 3/2(1+y)}} \tag{20}$$

As can be seen in Table 3, the assumption that P_{PCl_3} is negligible compared to the partial pressures of the other constituents, is a good assumption so that these other partial pressures do not need to be further modified. For $P_{PCl_3^o}$ values of 10^{-3} - 10^{-1} atm. and temperature values of 700-1000°C, the equilibrium P_{PCl_3} partial pressures range from a maximum of 6×10^{-8} atm. for $P_{PCl_3^o} = .1$ atm. and $T = 700°C$ to a minimum of 4×10^{-15} for $P_{PCl_3^o} = .001$ atm. and $T = 1000°C$. Note further that P_{PCl_3} for these temperature and pressure ranges is more sensitive to the pressure changes.

Table 3. The equilibrium PCl_3, HCl, PH_3, P_4, P_2, and H_2 partial pressures for PCl_3- H_2 mixtures at different temperatures and with different initial PCl_3 partial pressures, PCL30.

PCL30	T(°C)	PCL3	HCL	PH3	P4	P2	H2
.100E-02							
	700.	.846E-14	.300E-02	.164E-03	.162E-03	.944E-04	.9966
	800.	.763E-14	.300E-02	.117E-03	.920E-04	.258E-03	.9965
	900.	.592E-14	.300E-02	.719E-04	.276E-04	.409E-03	.9965
	1000.	.424E-14	.300E-02	.365E-04	.610E-05	.470E-03	.9965
.316E-02							
	700.	.414E-12	.949E-02	.229E-03	.639E-03	.188E-03	.9895
	800.	.386E-12	.949E-02	.172E-03	.459E-03	.576E-03	.9893
	900.	.323E-12	.949E-02	.118E-03	.205E-03	.111E-02	.9891
	1000.	.241E-12	.949E-02	.753E-04	.566E-04	.143E-02	.9890
.100E-01							
	700.	.193E-10	.300E-01	.300E-03	.225E-02	.352E-03	.9671
	800.	.185E-10	.300E-01	.233E-03	.186E-02	.116E-02	.9667
	900.	.166E-10	.300E-01	.172E-03	.114E-02	.263E-02	.9661
	1000.	.134E-10	.300E-01	.122E-03	.451E-03	.404E-02	.9654
.316E-01							
	700.	.941E-09	.949E-01	.359E-03	.749E-02	.643E-03	.8966
	800.	.916E-09	.949E-01	.283E-03	.673E-02	.220E-02	.8959
	900.	.864E-09	.949E-01	.217E-03	.508E-02	.555E-02	.8943
	1000.	.761E-09	.949E-01	.170E-03	.282E-02	.101E-01	.8921
.100E+00							
	700.	.618E-07	.300E+00	.283E-03	.243E-01	.116E-02	.6742
	800.	.609E-07	.300E+00	.225E-03	.229E-01	.407E-02	.6728
	900.	.594E-07	.300E+00	.175E-03	.195E-01	.109E-01	.6694
	1000.	.560E-07	.300E+00	.135E-03	.138E-01	.223E-01	.6637

C. Effect of Varying T_D

In order to calculate the equilibrium constituent partial pressures in the growth zone, one must know the input partial pressures. These include the HCl and InCl pressures from the source zone, P_{HCl^1} and P_{InCl^1}, the downstream HCl pressure, P_{HCl^2}, and the PH_3 pressure $P_{PH_3^o}$. These species are illustrated in Figure 8.

The deposition reaction is

$$InCl + \frac{1}{2}(1-3y)H_2 + (1-y)\ x/2\ P_2 + (1-y)(1-x)/4\ P_4 + yPH_3 \rightarrow InP(s) + HCl \tag{21}$$

where x is given by (17) and y is

$$y = \frac{P_{PH_3}}{P_{PH_3} + xP_{P_2} + (1-x)\ P_{P_4}} \quad . \tag{22}$$

For every mole of InCl consumed, one mole of new HCl must be formed so that

$$P_{InCl} = P_{InCl^1} - (P_{HCl} - P_{HCl^1} - P_{HCl^2}) = R - P_{HCl} \tag{23}$$

P_{PH_3} can be found from (12) where

$$\ln K_{12} = \ln \frac{P_{P_2}^{x/2}\ P_{P_4}^{(1-x)/4}\ P_{H_2}^{3/2}}{P_{PH_3}} = -\frac{\Delta G_{12}}{RT} \tag{24}$$

The total pressure is 1 atm. so

$$\begin{aligned} P_{H_2} &= 1 - P_{InCl} - P_{PH_3} - P_{P_2} - P_{P_4} - P_{HCl} \\ &= 1 - P_{InCl^1} - 2P_{HCl^1} - 2P_{HCl^2} - P_{PH_3^o} + P_{P_2} + 3P_{P_4} + P_{HCl} \\ &= S + HCl \end{aligned} \tag{25}$$

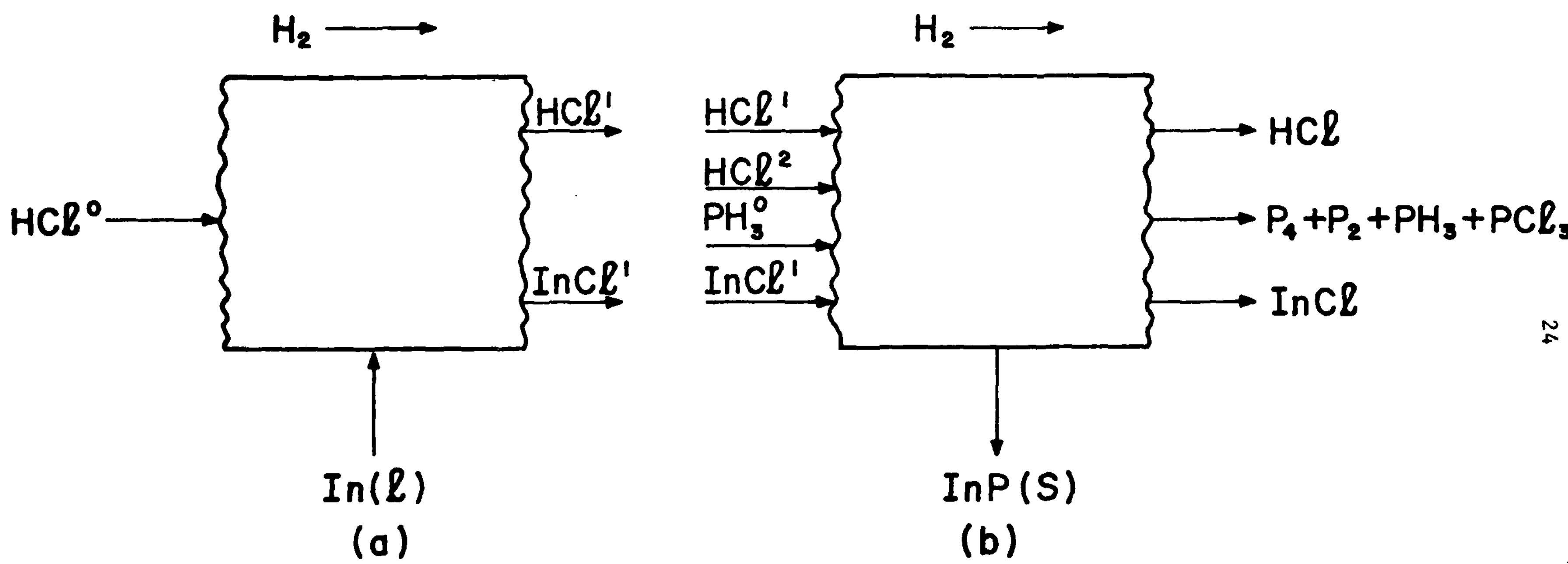


Fig. 8. The nomenclature used to describe the gases flowing into and out of (a) the source zone and (b) the deposition zone.

From (21)

$$K_{21} = P_{HCl}/(P_{InCl}P_{H_2}^{(1-3y)/2}\ P_{P_2}^{(1-y)x/2}\ P_{P_4}^{(1-y)(1-x)/4}\ P_{PH_3}^{y}$$

$$= P_{HCl}/\{(R-P_{HCl})(S+P_{HCl})^{(1-3y)/2}\ P_{P_2}^{(1-y)x/2}\ P_{P_4}^{(1-y)(1-x)/4}\ P_{PH_3}^{y}\}$$

$$= \exp\ (-\Delta G_{21}/RT)\ . \tag{26}$$

After a value of P_{P_4} has been assumed, P_{P_2} is determined from (13), P_{PH_3} is found from (24), P_{HCl} is computed from (26) by realizing that $S >> P_{HCl}$, P_{H_2} is calculated using (25), and P_{InCl} is found from (23). P_{PH_3} can also be computed from the phosphorous balance. For every mole of InP formed one mole of new HCl is formed and one mole of PH_3 is consumed. Thus,

$$P_{PH_3} = P_{PH_3^o} - 2P_{P_2} - 4P_{P_4} - (P_{HCl} - P_{HCl^1} - P_{HCl^2})\ . \tag{27}$$

The two values of P_{PH_3} are compared, and than a new value of P_{P_4} is assumed. This process continues until the two values are equal.

In Tables 4 and Figure 9, the InCl, HCl, PH_3, P_4, P_2 and H_2 concentrations in equilibrium with InP are computed as a function of the deposition temperature, T_D, for a source temperature, T_S, of 850°C, an initial source HCl pressure (HCLO) of 10^{-2} atm., an initial PH_3 (PH30) concentration of 10^{-2} atm., and downstream initial HCl pressures (HCL2) of 0 and 10^{-4} atm. There it is seen that the InCl concentration increases, or, conversely, the amount of InP being deposited decreases, as T_D increases until a temperature is reached where no InP is deposited. For $HCl^2 = 0$ this temperature is 822°C and for $HCl2 = 10^{-4}$ atm. it is 766°C. As the HCl2 concentration increases, the maximum

Table 4. The equilibrium InCl, HCl, PH_3, P_4, P_2 and H_2 partial pressures calculated for different deposition temperatures, T_D, when T_S = 850°C, HCl^o = .01 atm., and HCl^2 = a.) 0, and b.) 10^{-4} atm.

TS	HCLO	INCL1	HCL1	HCL2	PH30	P/IN
850.	.100E-01	.989E-02	.105E-03	0.	.100E-01	1.0107
T	INCL	HCL	PH3	P4	P2	H2
650.	.905E-02	.952E-03	.347E-03	.212E-02	.162E-03	.9874
654.	.910E-02	.902E-03	.344E-03	.213E-02	.172E-03	.9874
658.	.915E-02	.854E-03	.341E-03	.214E-02	.184E-03	.9873
662.	.919E-02	.809E-03	.338E-03	.214E-02	.196E-03	.9873
666.	.923E-02	.766E-03	.336E-03	.215E-02	.208E-03	.9873
670.	.927E-02	.725E-03	.333E-03	.215E-02	.222E-03	.9873
674.	.931E-02	.687E-03	.330E-03	.215E-02	.236E-03	.9873
678.	.935E-02	.651E-03	.326E-03	.216E-02	.250E-03	.9873
682.	.938E-02	.617E-03	.323E-03	.216E-02	.266E-03	.9873
686.	.941E-02	.585E-03	.320E-03	.216E-02	.282E-03	.9872
690.	.945E-02	.555E-03	.318E-03	.216E-02	.299E-03	.9872
694.	.947E-02	.526E-03	.315E-03	.216E-02	.317E-03	.9872
698.	.950E-02	.499E-03	.312E-03	.216E-02	.335E-03	.9872
702.	.953E-02	.474E-03	.309E-03	.215E-02	.354E-03	.9872
706.	.955E-02	.449E-03	.307E-03	.215E-02	.375E-03	.9872
710.	.957E-02	.427E-03	.303E-03	.215E-02	.396E-03	.9872
714.	.959E-02	.405E-03	.300E-03	.214E-02	.418E-03	.9871
718.	.962E-02	.385E-03	.298E-03	.214E-02	.441E-03	.9871
722.	.963E-02	.365E-03	.295E-03	.213E-02	.465E-03	.9871
726.	.965E-02	.347E-03	.292E-03	.212E-02	.490E-03	.9871
730.	.967E-02	.330E-03	.290E-03	.211E-02	.516E-03	.9871
734.	.969E-02	.314E-03	.287E-03	.210E-02	.543E-03	.9871
738.	.970E-02	.298E-03	.285E-03	.209E-02	.571E-03	.9870
742.	.972E-02	.283E-03	.282E-03	.208E-02	.600E-03	.9870
746.	.973E-02	.270E-03	.279E-03	.207E-02	.631E-03	.9870
750.	.974E-02	.257E-03	.276E-03	.206E-02	.662E-03	.9870
754.	.976E-02	.244E-03	.274E-03	.205E-02	.695E-03	.9870
758.	.977E-02	.232E-03	.272E-03	.204E-02	.729E-03	.9870
762.	.978E-02	.221E-03	.269E-03	.202E-02	.764E-03	.9869
766.	.979E-02	.211E-03	.266E-03	.201E-02	.800E-03	.9869
770.	.980E-02	.201E-03	.264E-03	.199E-02	.837E-03	.9869
774.	.981E-02	.191E-03	.261E-03	.198E-02	.876E-03	.9869
778.	.982E-02	.182E-03	.258E-03	.196E-02	.915E-03	.9869
782.	.983E-02	.174E-03	.256E-03	.194E-02	.956E-03	.9868
786.	.983E-02	.166E-03	.253E-03	.192E-02	.999E-03	.9868
790.	.984E-02	.158E-03	.251E-03	.190E-02	.104E-02	.9868
794.	.985E-02	.151E-03	.248E-03	.188E-02	.109E-02	.9868
798.	.986E-02	.144E-03	.246E-03	.186E-02	.113E-02	.9868
802.	.986E-02	.137E-03	.243E-03	.184E-02	.118E-02	.9867
806.	.987E-02	.131E-03	.240E-03	.182E-02	.123E-02	.9867
810.	.988E-02	.125E-03	.238E-03	.180E-02	.128E-02	.9867
814.	.988E-02	.119E-03	.236E-03	.177E-02	.133E-02	.9867
818.	.989E-02	.114E-03	.234E-03	.175E-02	.138E-02	.9866
822.	.989E-02	.109E-03	.232E-03	.172E-02	.143E-02	.9866

(a)

TS	HCLO	INCL1	HCL1	HCL2	PH30	P/IN
850.	.100E-01	.989E-02	.105E-03	.100E-03	.100E-01	1.0107
T	INCL	HCL	PH3	P4	P2	H2
650.	.914E-02	.964E-03	.348E-03	.214E-02	.162E-03	.9872
654.	.919E-02	.913E-03	.345E-03	.215E-02	.173E-03	.9872
658.	.924E-02	.864E-03	.342E-03	.216E-02	.185E-03	.9872
662.	.928E-02	.818E-03	.339E-03	.216E-02	.197E-03	.9872
666.	.932E-02	.775E-03	.336E-03	.217E-02	.210E-03	.9872
670.	.937E-02	.734E-03	.333E-03	.217E-02	.223E-03	.9872
674.	.940E-02	.696E-03	.330E-03	.218E-02	.237E-03	.9872
678.	.944E-02	.659E-03	.328E-03	.218E-02	.252E-03	.9871
682.	.948E-02	.625E-03	.324E-03	.218E-02	.267E-03	.9871
686.	.951E-02	.593E-03	.321E-03	.218E-02	.283E-03	.9871
690.	.954E-02	.562E-03	.319E-03	.218E-02	.300E-03	.9871
694.	.957E-02	.533E-03	.315E-03	.218E-02	.318E-03	.9871
698.	.959E-02	.505E-03	.312E-03	.218E-02	.337E-03	.9871
702.	.962E-02	.479E-03	.310E-03	.218E-02	.356E-03	.9871
706.	.964E-02	.455E-03	.307E-03	.217E-02	.377E-03	.9870
710.	.967E-02	.432E-03	.305E-03	.217E-02	.398E-03	.9870
714.	.969E-02	.410E-03	.301E-03	.216E-02	.420E-03	.9870
718.	.971E-02	.389E-03	.298E-03	.216E-02	.443E-03	.9870
722.	.973E-02	.370E-03	.296E-03	.215E-02	.467E-03	.9870
726.	.9[illegible]5E-02	.352E-03	.293E-03	.214E-02	.493E-03	.9870
730.	.9[illegible]7E-02	.334E-03	.291E-03	.214E-02	.519E-03	.9870
734.	.978E-02	.318E-03	.288E-03	.213E-02	.546E-03	.9869
738.	.980E-02	.302E-03	.285E-03	.212E-02	.574E-03	.9869
742.	.981E-02	.287E-03	.282E-03	.211E-02	.604E-03	.9869
746.	.983E-02	.273E-03	.280E-03	.210E-02	.634E-03	.9869
750.	.984E-02	.260E-03	.277E-03	.208E-02	.666E-03	.9869
754.	.985E-02	.247E-03	.275E-03	.207E-02	.699E-03	.9869
758.	.986E-02	.235E-03	.272E-03	.206E-02	.733E-03	.9868
762.	.988E-02	.224E-03	.270E-03	.204E-02	.768E-03	.9868
766.	.989E-02	.213E-03	.267E-03	.203E-02	.804E-03	.9868

(b)

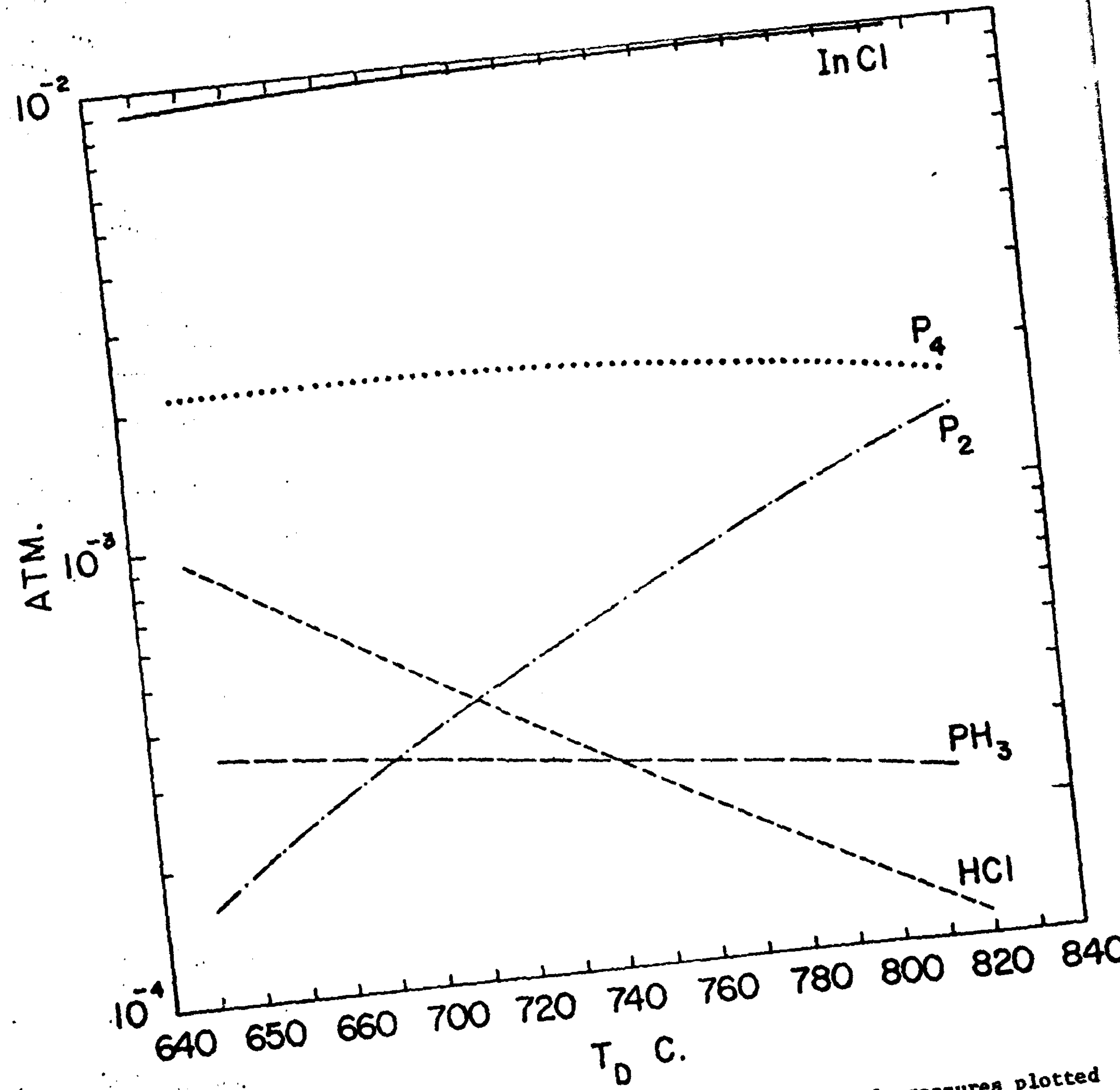


Fig. 9. The InCl, HCl, PH_3, P_4 and P_2 equilibrium partial pressures plotted as a function of the deposition temperature, T_D, when $T_S = 850°C$, HCl^o = .01 atm., $HCl^2 = 0$, and PH_3^o = .01 atm.

deposition temperature decreases due to the fact that HCl is generated by the InP deposition process (Eq. (21)). Clearly, if the HCl2 concentration is too high at a given deposition temperature, the InP will evaporate instead of deposit.

The other trends with increasing deposition temperature are P_{HCl} decreases, P_{P_2} increases, and P_{P_4} and P_{PH_3} do not change much. P_{HCl} decreases due to the fact that there is less InP deposition. Because there is less InP deposited, there is more phosphorous in the vapor phase, and most of the extra phosphorous is taken up by P_2 since P_4 and PH_3 have a greater tendency to dissociate as the temperature is increased.

The fraction of the indium that is deposited under equilibrium conditions, f_{In}, is determined rather than the equilibrium growth rate because more insight into the thermodynamics can be obtained. For example, the growth rate does not distinguish between changes produced by altering the flow rates and those produced by altering the free energy. Also, the deposition rate can be obtained from f_{In} by multiplying it by the number of atoms per unit volume in the gas phase, the input HCl input pressure and flow rate, and the fraction ($\sim$.99) of the HCl^o converted to InCl in the source zone, $InCl^1$, and dividing the product by the number of atoms of indium per unit volume in InP. The equation for f_{In} is simply

$$f_{In} = \frac{P_{InCl^1} - P_{InCl}}{P_{InCl^1}} \tag{28}$$

where P_{InCl} is the equilibrium InCl partial pressure in the deposition zone. The values of P_{InCl} and P_{InCl^1} are those which were computed

for the standard conditions which are: $T_s = 850°C$, $T_D = 700°C$, $P_{HCl^o} = .01$ atm., $P_{PH_3^o} = .01$ atm., and P_{HCl^2} is either 0 or 10^{-4} atm.

Increasing the deposition tempera[illegible] also causes f_{In} to decrease because it drives the deposition reaction to the left. It is shown in Figure 10 and Table 5 that at 650°C $f_{In} = .0856$ and it decreases to 0 at $T = 825°C$ when no HCl^2 is present, but these values are reduced when $P_{HCl^2} = 10^{-4}$ atm. At 650°C $f_{In} = .0766$ and the temperature for which it is zero is 768°C.

D. The Effect of Varying HCl^o

The equations used in this section are the same as those used in the previous section. The only difference is that P_{HCl^o} is varied instead of T_D. In Figure 11 and Tables 6a and b the input HCl pressure is varied from .001 to .1, and again the equilibrium InCl, HCl, PH_3, P_4, P_2 and H_2 pressures are determined for $T_s = 850°C.$, $T_D = 700°C$, $P_{PH_3^o} = .01$ atm., and $P_{HCl^2} = 0$ or 10^{-4} atm.

The plot and Table 6a show that P_{InCl} and P_{HCl} increase almost linearly whereas the pressures of the phosphorus containing compounds decrease slightly. P_{InCl} increases almost linearly since the source reaction is ∿99% efficient over a wide range of temperatures and pressures. For the same reason P_{HCl} increases almost linearly. There is a small additional increase in P_{HCl} due to the fact that a greater percent of the indium is deposited as InP. That a bit more InP is deposited also accounts for the slight decreases in the pressures of the phosphorous containing compounds.

In Table 6b it is seen that adding HCl downstream increases P_{HCl} only slightly. This is due to the fact that the added HCl drives the deposition reaction (21) to the left. The effect of the HCl is so great

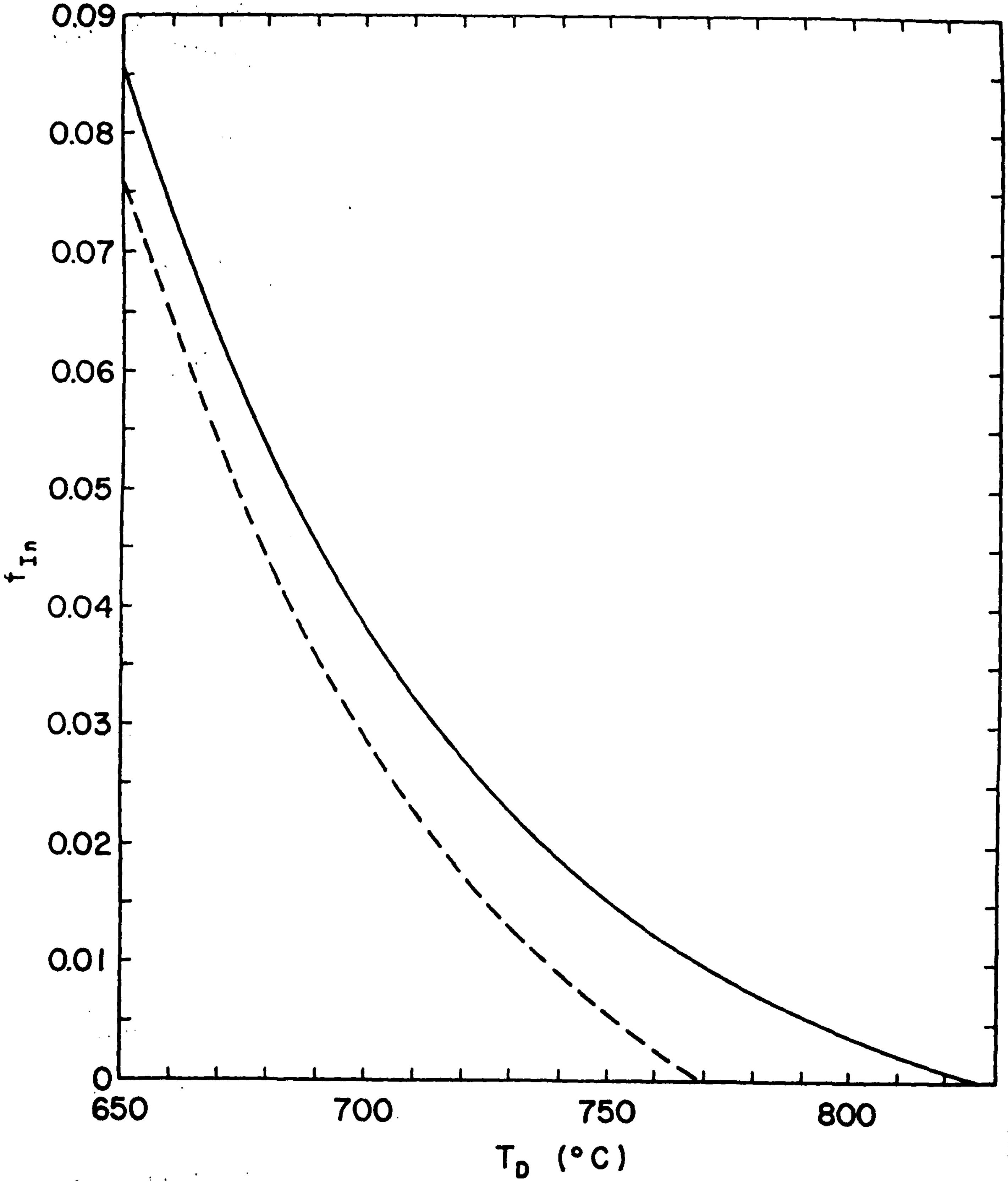


Fig. 10. The fraction of indium deposited, f_{In}, plotted as a function of the deposition temperature, T_D, when the downstream HCl concentration is 0(———) and 10^{-4} atm. (-----).

Table 5. **The equilibrium InCl partial pressure in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited, f_{In}, for different deposition temperatures, T_D, when the downstream HCl concentrations are 0 and 10^{-4} atm.**

TS	PH30	HCL2	HCL0	HCL2	
850.	0.	0.0000	.01	.0001	
TD	INCL1	INCL	f_{In}	INCL	f_{In}
650.	.9895E-02	.9048E-02	.0856	.9136E-02	.0766
654.	.9895E-02	.9098E-02	.0805	.9187E-02	.0715
658.	.9895E-02	.9146E-02	.0756	.9236E-02	.0666
662.	.9895E-02	.9191E-02	.0711	.9282E-02	.0620
666.	.9895E-02	.9234E-02	.0667	.9325E-02	.0576
670.	.9895E-02	.9275E-02	.0627	.9366E-02	.0535
674.	.9895E-02	.9313E-02	.0588	.9404E-02	.0496
678.	.9895E-02	.9349E-02	.0552	.9441E-02	.0459
682.	.9895E-02	.9383E-02	.0517	.9475E-02	.0424
686.	.9895E-02	.9415E-02	.0485	.9507E-02	.0391
690.	.9895E-02	.9445E-02	.0454	.9538E-02	.0360
694.	.9895E-02	.9474E-02	.0425	.9567E-02	.0331
698.	.9895E-02	.9501E-02	.0398	.9595E-02	.0303
702.	.9895E-02	.9526E-02	.0372	.9621E-02	.0277
706.	.9895E-02	.9551E-02	.0348	.9645E-02	.0252
710.	.9895E-02	.9573E-02	.0325	.9668E-02	.0229
714.	.9895E-02	.9595E-02	.0303	.9690E-02	.0207
718.	.9895E-02	.9615E-02	.0282	.9711E-02	.0186
722.	.9895E-02	.9635E-02	.0263	.9730E-02	.0166
726.	.9895E-02	.9653E-02	.0244	.9748E-02	.0148
730.	.9895E-02	.9670E-02	.0227	.9766E-02	.0130
734.	.9895E-02	.9686E-02	.0210	.9782E-02	.0113
738.	.9895E-02	.9702E-02	.0195	.9798E-02	.0097
742.	.9895E-02	.9717E-02	.0180	.9813E-02	.0083
746.	.9895E-02	.9730E-02	.0166	.9827E-02	.0068
750.	.9895E-02	.9743E-02	.0153	.9840E-02	.0055
754.	.9895E-02	.9756E-02	.0140	.9853E-02	.0042
758.	.9895E-02	.9768E-02	.0128	.9865E-02	.0030
762.	.9895E-02	.9779E-02	.0117	.9876E-02	.0019
766.	.9895E-02	.9789E-02	.0106	.9887E-02	.0008
770.	.9895E-02	.9799E-02	.0096		
774.	.9895E-02	.9809E-02	.0087		
778.	.9895E-02	.9818E-02	.0078		
782.	.9895E-02	.9826E-02	.0069		
786.	.9895E-02	.9834E-02	.0061		
790.	.9895E-02	.9842E-02	.0053		
794.	.9895E-02	.9849E-02	.0046		
798.	.9895E-02	.9856E-02	.0039		
802.	.9895E-02	.9863E-02	.0032		
806.	.9895E-02	.9869E-02	.0026		
810.	.9895E-02	.9875E-02	.0020		
814.	.9895E-02	.9881E-02	.0014		
818.	.9895E-02	.9886E-02	.0008		
822.	.9895E-02	.9891E-02	.0[illegible]		

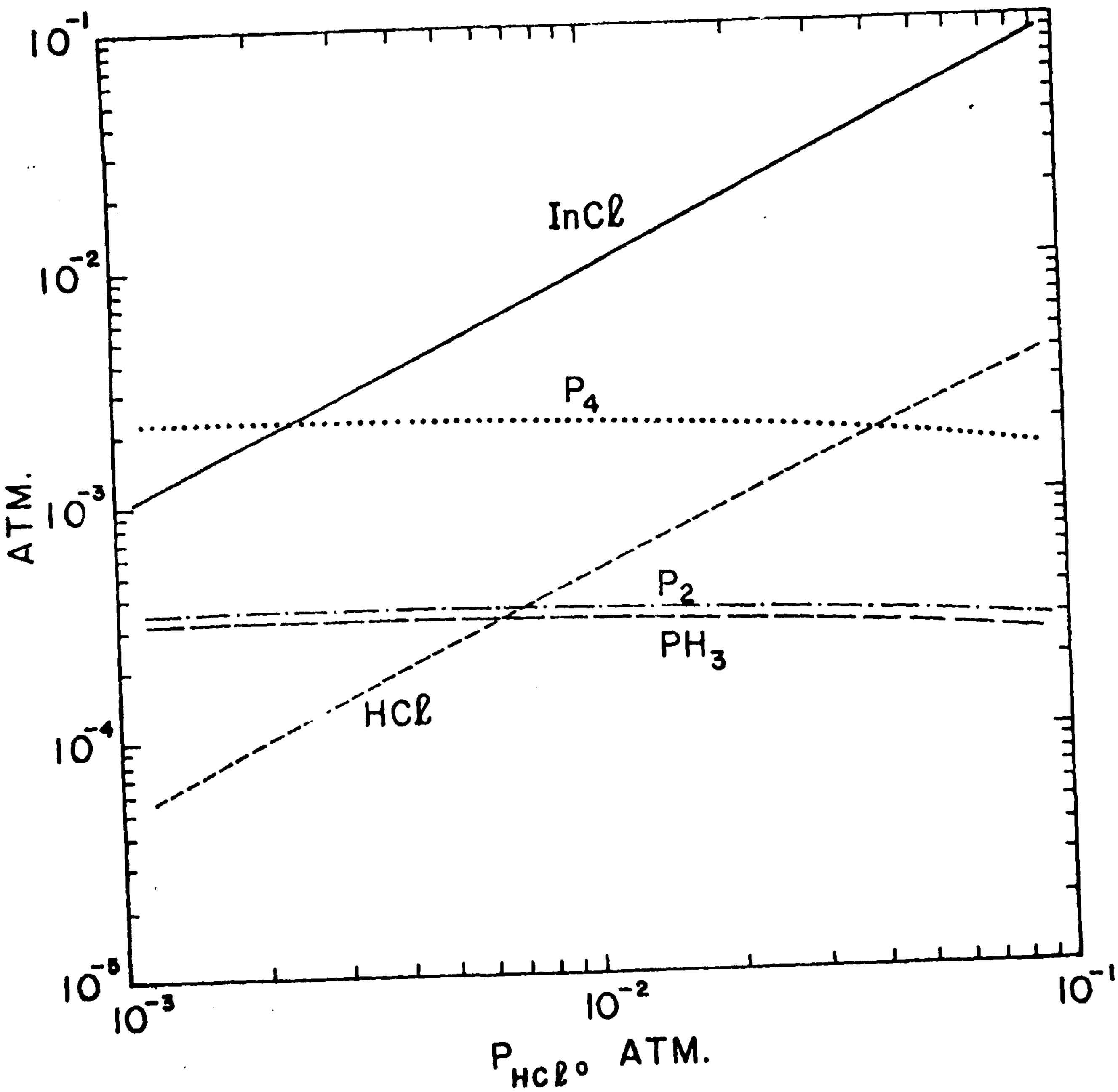


Fig. 11. The InCl, HCl, PH_3, P_4, and P_2 equilibrium partial pressures plotted as a function of the source input HCl concentration, HCl^o when T_S = 850°C, T_D = 700°C, PH_3^o = .01 atm., and HCl^2 = 0.

Table 6. The equilibrium InCl, HCl, PH_3, P_4, P_2 and H_2 partial pressures calculated for different source input HCl concentrations, HCl^o, when $T_S = 850°C$, $T_D = 700°C$, $PH_3^o = .01$ atm. and HCl^2 = a.) 0 and b.) 10^{-4} atm.

TS	TD	HCL2	PH30			
850.	700.	0.	.100E-01			
HCLO	INCL	HCL	PH3	P4	P2	H2
.100E+00	.959E-01	.407E-02	.248E-03	.153E-02	.290E-03	.8979
.912E-01	.875E-01	.372E-02	.249E-03	.148E-02	.286E-03	.9068
.832E-01	.797E-01	.345E-02	.254E-03	.153E-02	.291E-03	.9147
.759E-01	.727E-01	.319E-02	.260E-03	.159E-02	.296E-03	.9220
.692E-01	.662E-01	.295E-02	.265E-03	.163E-02	.300E-03	.9286
.631E-01	.604E-01	.273E-02	.269E-03	.168E-02	.304E-03	.9347
.575E-01	.550E-01	.252E-02	.273E-03	.172E-02	.308E-03	.9402
.525E-01	.502E-01	.232E-02	.276E-03	.176E-02	.312E-03	.9452
.479E-01	.457E-01	.214E-02	.280E-03	.180E-02	.315E-03	.9497
.437E-01	.417E-01	.197E-02	.284E-03	.184E-02	.318E-03	.9539
.398E-01	.380E-01	.181E-02	.286E-03	.187E-02	.321E-03	.9577
.363E-01	.346E-01	.166E-02	.289E-03	.190E-02	.323E-03	.9612
.331E-01	.316E-01	.152E-02	.292E-03	.193E-02	.326E-03	.9643
.302E-01	.288E-01	.140E-02	.294E-03	.195E-02	.328E-03	.9672
.275E-01	.263E-01	.128E-02	.296E-03	.198E-02	.330E-03	.9699
.251E-01	.239E-01	.118E-02	.298E-03	.200E-02	.332E-03	.9723
.229E-01	.218E-01	.108E-02	.300E-03	.202E-02	.334E-03	[illegible]
.209E-01	.199E-01	.986E-03	.301E-03	.204E-02	.335E-03	[illegible]
[illegible]	.182E-01	.903E-03	.303E-03	.206E-02	.337E-03	.9783
.174E-01	.166E-01	.826E-03	.304E-03	.207E-02	.338E-03	.9799
.158E-01	.151E-01	.756E-03	.305E-03	.209E-02	.339E-03	.9814
.145E-01	.138E-01	.691E-03	.306E-03	.210E-02	.340E-03	.9828
.132E-01	.126E-01	.632E-03	.308E-03	.211E-02	.341E-03	.9841
.120E-01	.114E-01	.578E-03	.308E-03	.212E-02	.342E-03	.9852
.110E-01	.104E-01	.528E-03	[illegible]	.213E-02	.343E-03	.9862
.100E-01	.952E-02	.483E-03	.311E-03	.214E-02	.344E-03	.9872
.912E-02	.868E-02	.441E-03	.311E-03	.215E-02	.344E-03	.9881
.832E-02	.791E-02	.403E-03	.312E-03	.216E-02	.345E-03	.9889
.759E-02	.722E-02	.368E-03	.312E-03	.217E-02	.346E-03	.9896
.692E-02	.658E-02	.336E-03	.313E-03	.217E-02	.346E-03	.9902
.631E-02	.600E-02	.307E-03	.313E-03	.218E-02	.347E-03	.9909
.575E-02	.547E-02	.280E-03	.314E-03	.219E-02	.347E-03	.9914
.525E-02	.499E-02	.256E-03	.314E-03	.219E-02	.348E-03	.9919
.479E-02	.455E-02	.234E-03	.314E-03	.220E-02	.348E-03	.9924
.437E-02	.415E-02	.213E-03	.314E-03	.220E-02	.348E-03	.9928
.398E-02	.379E-02	.195E-03	.315E-03	.220E-02	.349E-03	.9932
.363E-02	.345E-02	.178E-03	.315E-03	.221E-02	.349E-03	.9935
.331E-02	.315E-02	.162E-03	.315E-03	.221E-02	.349E-03	.9938
.302E-02	.287E-02	.148E-03	.315E-03	.221E-02	.349E-03	.9941
275E-02	.262E-02	.135E-03	.317E-03	.222E-02	.349E-03	.9944
.251E-02	.239E-02	.123E-03	.317E-03	.222E-02	.350E-03	.9946
.229E-02	.218E-02	.112E-03	.317E-03	.222E-02	.350E-03	.9948
.209E-02	.199E-02	.102E-03	.316E-03	.222E-02	.350E-03	.9950
.191E-02	.181E-02	.935E-04	.317E-03	.222E-02	.350E-03	.9952
.174E-02	.165E-02	.853E-04	.317E-03	.223E-02	.350E-03	.9954
.158E-02	.151E-02	.778E-04	.318E-03	.223E-02	.350E-03	.9955
.145E-02	.137E-02	.710E-04	.318E-03	.223E-02	.351E-03	.9957
.132E-02	.125E-02	.648E-04	.318E-03	.223E-02	.351E-03	.9958
.120E-02	.114E-02	.591E-04	.318E-03	.223E-02	.351E-03	.9959
.110E-02	.104E-02	.539E-04	.317E-03	.223E-02	.351E-03	.9960

(a)

TS	TD	HCL2	PH30			
850.	700.	.100E-03	.100E-01			
HCLO	INCL	HCL	PH3	P4	P2	H2
.100E+00	.961E-01	.402E-02	.244E-03	.144E-02	.282E-03	.8979
.912E-01	.876E-01	.373E-02	.250E-03	.150E-02	.288E-03	.9067
.832E-01	.798E-01	.346E-02	.256E-03	.155E-02	.293E-03	.9146
.759E-01	.728E-01	.321E-02	.260E-03	.161E-02	.298E-03	.9215
.692E-01	.663E-01	.297E-02	.265E-03	.165E-02	.302E-03	.9285
.631E-01	.605E-01	.274E-02	.270E-03	.1[illegible]0E-02	.306E-03	.9345
.575E-01	.551E-01	.253E-02	.274E-03	.174E-02	.310E-03	.9400
.525E-01	.503E-01	.233E-02	.278E-03	.179E 02	.314E-03	.9450
.479E-01	.458E-01	.215E-02	.281E-03	.182E-02	.317E-03	.9496
.437E-01	.418E-01	.197E-02	.284E-03	.1[illegible]E-02	.320E-03	.9538
.398E-01	.381E-01	.182E-02	.287E-03	.189E-02	.323E-03	.9576
.363E-01	.347E-01	.167E-02	.290E-03	.192E-02	.325E-03	.9611
.331E-01	.317E-01	.153E-02	.293E-03	.195E-02	.328E-03	.9642
.302E-01	.289E-01	.141E-02	.294E-03	.197E-02	.330E-03	.9671
.275E-01	.264E-01	.129E-02	.297E-03	.200E-02	.332E-03	.9697
.251E-01	.240E-01	.118E-02	.299E-03	.202E-02	.334E-03	.9721
.229E-01	.219E-01	.108E-02	.301E-03	.204E-02	.335E-03	.9743
.209E-01	.200E-01	.993E-03	.302E-03	.206E-02	.337E-03	.9763
.191E-01	.182E-01	.910E-03	.303E-03	.208E-02	.338E-03	.9781
.174E-01	.166E-01	.833E-03	.305E-03	.209E-02	.340E-03	.9798
.158E-01	.152E-01	.762E-03	.306E-03	.211E-02	.341E-03	.9813
.145E-01	.139E-01	.698E-03	.307E-03	.212E-02	.342E-03	.9827
.132E-01	.126E-01	.638E-03	.308E-03	.213E-02	.343E-03	.9839
.120E-01	.115E-01	.584E-03	.309E-03	.215E-02	.344E-03	.9851
.110E-01	.105E-01	.534E-03	.310E-03	.216E-02	.345E-03	.9861
.100E-01	.961E-02	.489E-03	.311E-03	.217E-02	.345E-03	.9871
.912E-02	.877E-02	.447E-03	.312E-03	.217E-02	.346E-03	.9879
.832E-02	.801E-02	.409E-03	.313E-03	.218E-02	.347E-03	.9887
.759E-02	.731E-02	.374E-03	.312E-03	.219E-02	.347E-03	.9895
.692E-02	.668E-02	.342E-03	.314E-03	.220E-02	.348E-03	.9901
.631E-02	.610E-02	.312E-03	.314E-03	.220E-02	.348E-03	.9907
.575E-02	.557E-02	.286E-03	.315E-03	.221E-02	.349E-03	.9913
.525E-02	.509E-02	.261E-03	.315E-03	.221E-02	.349E-03	.9918
.479E-02	.465E-02	.239E-03	.315E-03	.222E-02	.350E-03	.9922
.437E-02	.425E-02	.219E-03	.316E-03	.222E-02	.350E-03	.9926
.398E-02	.388E-02	.200E-03	.316E-03	.223E-02	.350E-03	.9930
.363E-02	.355E-02	.183E-03	.316E-03	.223E-02	.351E-03	.9934
.331E-02	.324E-02	.167E-03	.317E-03	.223E-02	.351E-03	.9937
.302E-02	.297E-02	.153E-03	.317E-03	.224E-02	.351E-03	.9940
.275E-02	.271E-02	.140E-03	.317E-03	.224E-02	.351E-03	.9942
.251E-02	.248E-02	.128E-03	.317E-03	.224E-02	.351E-03	.9945
.229E-02	.227E-02	.118E-03	.317E-03	.224E-02	.352E-03	.9947

(b)

that for every HCl molecule added downstream, almost one less InP 'molecule' is deposited and therefore one less HCl molecule is created.

The effect of the downstream HCl is so strong that small amounts of it can completely stop the deposition. In Table 5b it is seen that this condition is reached when $P_{HCl^o} = 2.3 \times 10^{-3}$ atm. if $P_{HCl^2} = 10^{-4}$ atm.

In Figure 12 and Table 7 one sees that f_{In} changes very little as the input HCl pressure is varied from .001 to .1 atm and $P_{HCl^2} = 0$. This can be explained by the fact that the deposition input HCl, HCl^1, and $InCl^1$ concentrations increase at about the same rate since ~99% of the HCl^o is converted into InCl for all values of P_{HCl^o}. The increased InCl concentration in the deposition zone drives the deposition reaction to the right whereas the increased HCl concentration drives the reaction to the left. These effects essentially cancel each other. This is not the case for small P_{HCl^o} values when $P_{HCl^2} = 10^{-4}$ atm because now the HCl from both sources - HCl^1 and HCl^2 - have comparable values when $P_{HCl^o} = .01$ atm., and $P_{HCl^2} > P_{HCl^1}$ for smaller P_{HCl^o} values. As a result the effects of the HCl^2 dominate at the smaller HCl^o pressures and drive f_{In} to zero for $P_{HCl^o} \leq 2.4 \times 10^{-3}$ atm.

E. The Effects of Varying PH_3^o

The effects of varying the input PH_3 pressure are illustrated in Figures 13 and 14 and in Tables 8 and 9. In Figure 13 the constituent partial pressures are plotted as a function of PH_3^o and there it is seen that P_{InCl} dips ever so slightly, P_{HCl} increases slowly, and the partial pressures of the phosphorous containing compounds increase with the increase in P_{P_4} being the most rapid. P_{InCl} dips slightly due to the fact that more InP is deposited as PH_3^o increases. For the same

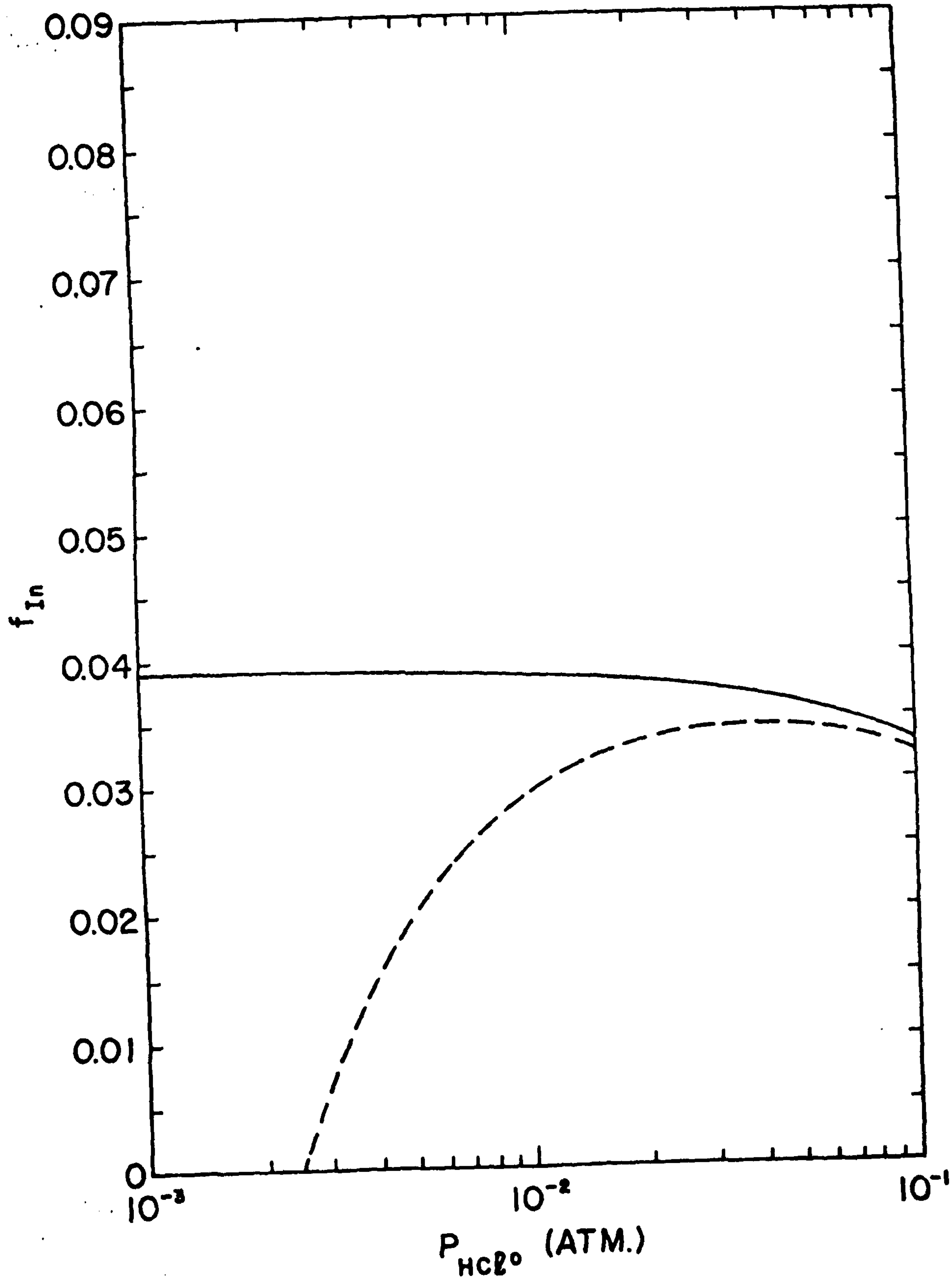


Fig. 12. The fraction of indium deposited, f_{In}, plotted as a function of the input HCl concentration, P_{HCl^o}, when the downstream HCl pressure is 0 (———) and 10^{-4} atm. (-----).

Table 7. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited, f_{In}, for different input HCl partial pressures, HCLO, when the downstream HCl concentrations are 0 and 10^{-4} atm.

TS	TD	HCL2	PH30	HCL2	
850.	700.	0.0000	.01	.0001	
HCLO	INCL1	INCL	f_{In}	INCL	f_{In}
.100E+00	.9899E-01	.9575E-01	.0328	.9583E-01	.0320
.912E-01	.9028E-01	.8727E-01	.0333	.8735E-01	.0324
.832E-01	.8233E-01	.7955E-01	.0338	.7963E-01	.0328
.759E-01	.7508E-01	.7251E-01	.0343	.7260E-01	.0331
.692E-01	.6848E-01	.6610E-01	.0347	.6619E-01	.0334
.631E-01	.6245E-01	.6026E-01	.0351	.6035E-01	.0337
.575E-01	.5695E-01	.5494E-01	.0354	.5502E-01	.0339
.525E-01	.5194E-01	.5008E-01	.0357	.5017E-01	.0340
.479E-01	.4737E-01	.4566E-01	.0360	.4575E-01	.0341
.437E-01	.4320E-01	.4163E-01	.0363	.4172E-01	.0342
.398E-01	.3940E-01	.3796E-01	.0365	.3805E-01	.0342
.363E-01	.3593E-01	.3461E-01	.0368	.3470E-01	.0342
.331E-01	.3277E-01	.3156E-01	.0370	.3165E-01	.0342
.302E-01	.2988E-01	.2877E-01	.0372	.2887E-01	.0341
.275E-01	.2725E-01	.2624E-01	.0373	.2633E-01	.0340
.251E-01	.2486E-01	.2392E-01	.0375	.2402E-01	.0338
.229E-01	.2267E-01	.2182E-01	.0376	.2191E-01	.0336
.209E-01	.2067E-01	.1989E-01	.0378	.1999E-01	.0333
.191E-01	.1885E-01	.1814E-01	.0379	.1825E-01	.0330
.174E-01	.1720E-01	.1654E-01	.0380	.1664E-01	.0326
.1[illegible]E-01	.1568E-01	.1508E-01	.0381	.[illegible]18E-01	.0322
.145E-01	.1430E-01	.1376E-01	.0382	.1385E-01	.0317
.132E-01	.1304E-01	.1254E-01	.0383	.1264E-01	.0311
.120E-01	.1190E-01	.1144E-01	.0384	.1153E-01	.0305
.110E-01	.1085E-01	.1043E-01	.0384	.1053E-01	.0298
.100E-01	.9895E-02	.9514E-02	.0385	.9608E-02	.0290
.912E-02	.9024E-02	.8676E-02	.0385	.8770E-02	.0281
.832E-02	.8230E-02	.7912E-02	.0386	.8006E-02	.0272
.759E-02	.7506E-02	.7216E-02	.0386	.7310E-02	.0261
.692E-02	.6845E-02	.6580E-02	.0387	.6675E-02	.0249
.631E-02	.6243E-02	.6001E-02	.0387	.6096E-02	.0236
.575E-02	.5694E-02	.5473E-02	.0388	.5567E-02	.0222
.525E-02	.5193E-02	.4991E-02	.0388	.5086E-02	.0206
.479E-02	.4736E-02	.4552E-02	.0388	.4646E-02	.0189
.437E-02	.4319E-02	.4151E-02	.0389	.4246E-02	.0169
.398E-02	.3939E-02	.3786E-02	.0389	.3880E-02	.0149
.363E-02	.3592E-02	.3453E-02	.0389	.3547E-02	.0125
.331E-02	.3276E-02	.3149E-02	.0389	.3243E-02	.0100
.302E-02	.2988E-02	.2872E-02	.0389	.2966E-02	.0072
.275E-02	.2725E-02	.2619E-02	.0389	.2714E-02	.0042
.251E-02	.2485E-02	.2388E-02	.0390	.2483E-02	.0008
.229E-02	.2267E-02	.2178E-02	.0390		
.209E-02	.2067E-02	.1987E-02	.0390		
.191E-02	.1885E-02	.1812E-02	.0390		
.174E-02	.1719E-02	.1652E-02	.0390		
.158E-02	.1568E-02	.1507E-02	.0390		
.145E-02	.1430E-02	.1374E-02	.0390		
.132E-02	.1304E-02	.1253E-02	.0390		
.120E-02	.1190E-02	.1143E-02	.0391		
.110E-02	.1085E-02	.1042E-02	.0391		

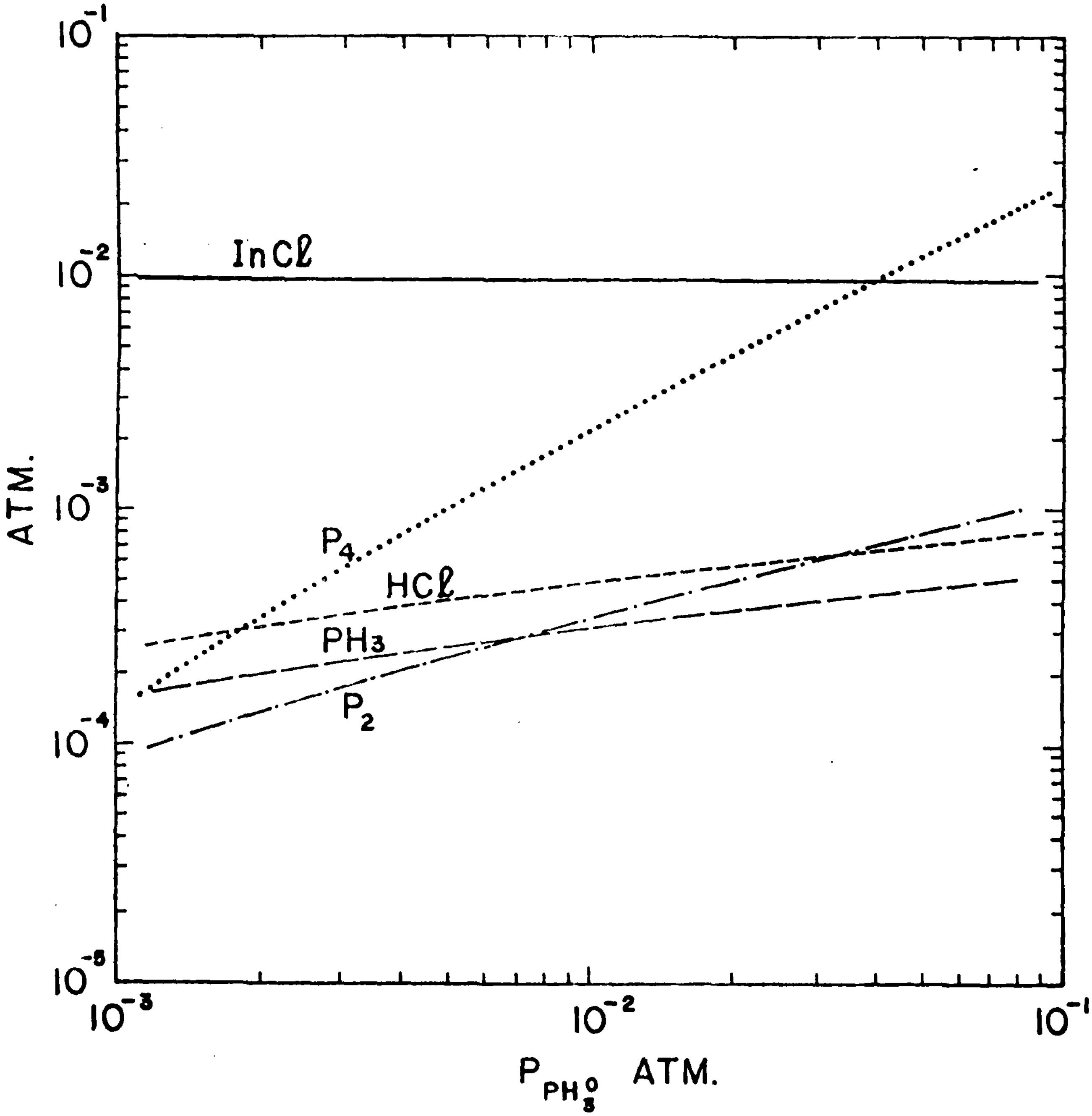


Fig. 13. The InCl, HCl, PH_3, P_4, and P_2 equilibrium partial pressures plotted as a function of the input PH_3 concentration, PH_3^o when T_S = 850°C, T_D = 700°C, HCl^o = .01 atm., and HCl^2 = 0.

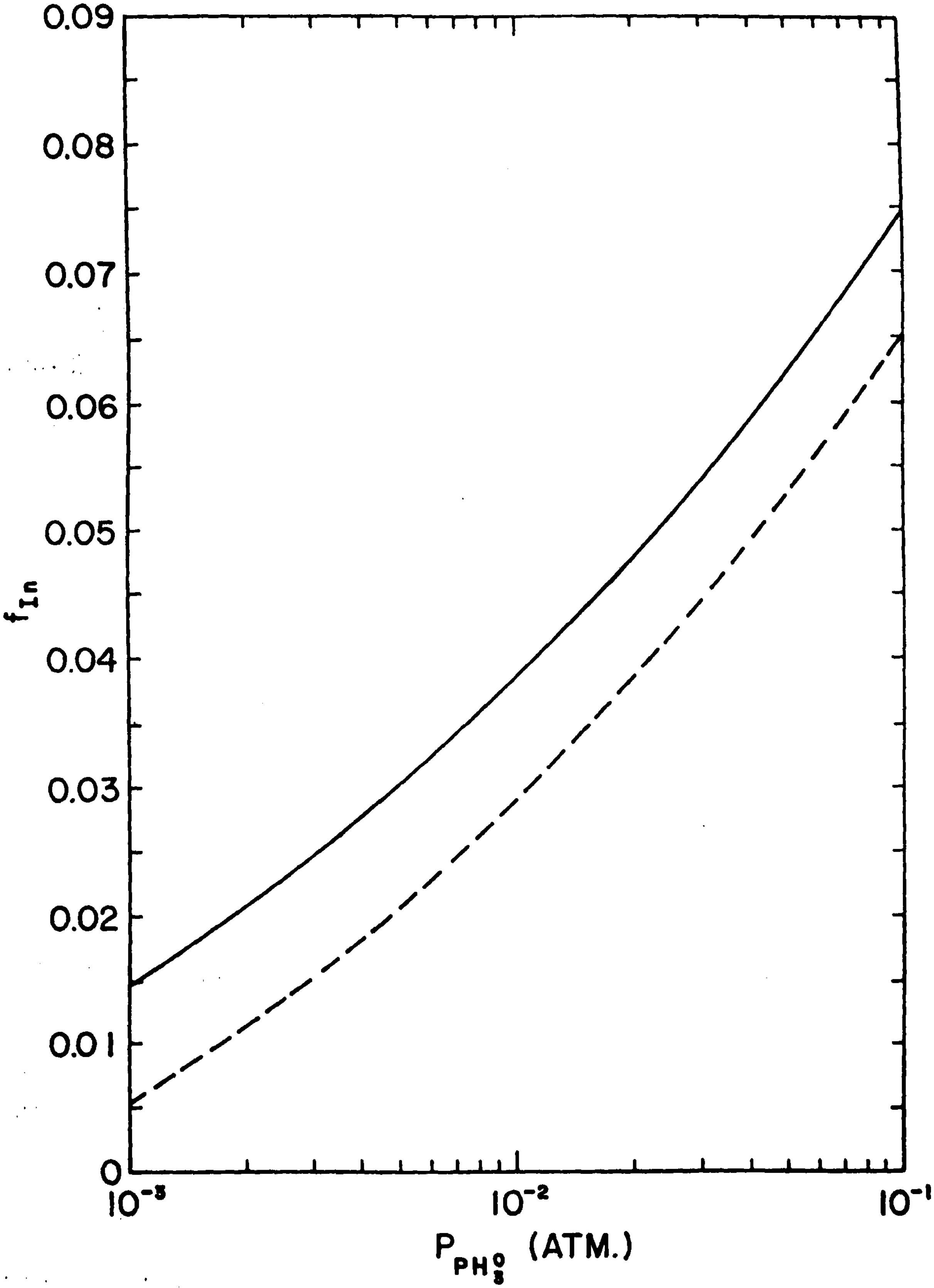


Fig. 14. The fraction of indium deposited, f_{In}, plotted as a function of the input PH_3 partial pressure, $P_{PH_3^o}$, when the downstream HCl concentration is 0 (———) and 10^{-4} atm. (------).

Table 8. The equilibrium InCl, HCl, PH_3, P_4, P_2 and H_2 partial pressures calculated for different input PH_3 concentrations, PH_3^o, when T_S = 850°C, T_D = 700°C, HCl^o = .01 atm., and HCl^2 = a.) 0, and b.) 10^{-4}.

TS	HCLO	INCL1	HCL1	HCL2	TD
850.	.100E-01	.989E-02	.105E-03	0.	700.

PH30	INCL	HCL	PH3	P4	P2	H2
.100E+ 0	.915E-02	.846E-03	.555E-03	.241E-01	.115E-02	.9642
.912E-01	.917E-02	.828E-03	.544E-03	.219E-01	.110E-02	.9664
.832E-01	.919E-02	.811E-03	.531E-03	.200E-01	.105E-02	.9685
.759E-01	.921E-02	.795E-03	.518E-03	.182E-01	.100E-02	.9703
.692E-01	.922E-02	.778E-03	.511E-03	.165E-01	.954E-03	.9720
.631E-01	.924E-02	.762E-03	.495E-03	.150E-01	.910E-03	.9736
.575E-01	.925E-02	.746E-03	.483E-03	.137E-01	.868E-03	.9750
.525E-01	.927E-02	.730E-03	.475E-03	.124E-01	.828E-03	.9763
.479E-01	.929E-02	.715E-03	.464E-03	.113E-01	.789E-03	.9774
.437E-01	.930E-02	.699E-03	.455E-03	.103E-01	.753E-03	.9785
.398E-01	.932E-02	.684E-03	.443E-03	.934E-02	.717E-03	.9795
.363E-01	.933E-02	.669E-03	.435E-03	.849E-02	.684E-03	.9804
.331E-01	.935E-02	.655E-03	.425E-03	.771E-02	.652E-03	.9812
.302E-01	.936E-02	.641E-03	.415E-03	.700E-02	.621E-03	.9820
.275E-01	.937E-02	.626E-03	.405E-03	.636E-02	.592E-03	.9826
.251E-01	.939E-02	.613E-03	.397E-03	.577E-02	.564E-03	.9833
.229E-01	.940E-02	.599E-03	.386E-03	.524E-02	.537E-03	.9838
.209E-01	.941E-02	.586E-03	.377E-03	.475E-02	.512E-03	.9844
.191E-01	.943E-02	.572E-03	.368E-03	.431E-02	.487E-03	.9848
.174E-01	.944E-02	.559E-03	.359E-03	.391E-02	.464E-03	.9853
.158E-01	.945E-02	.547E-03	.352E-03	.354E-02	.442E-03	.9857
.145E-01	.947E-02	.534E-03	.343E-03	.321E-02	.421E-03	.9860
.132E-01	.948E-02	.522E-03	.334E-03	.291E-02	.400E-03	.9864
.120E-01	.949E-02	.510E-03	.326E-03	.263E-02	.381E-03	.9867
.110E-01	.950E-02	.498E-03	.318E-03	.238E-02	.362E-03	.9869
.100E-01	.951E-02	.486E-03	.311E-03	.215E-02	.345E-03	.9872
.912E-02	.953E-02	.475E-03	.303E-03	.195E-02	.328E-03	.9874
.832E-02	.954E-02	.463E-03	.296E-03	.176E-02	.311E-03	.9876
.759E-02	.955E-02	.452E-03	.288E-03	.159E-02	.296E-03	.9878
.692E-02	.956E-02	.441E-03	.281E-03	.143E-02	.281E-03	.9880
.631E-02	.957E-02	.431E-03	.274E-03	.129E-02	.267E-03	.9882
.575E-02	.958E-02	.420E-03	.267E-03	.117E-02	.254E-03	.9883
.525E-02	.959E-02	.410E-03	.260E-03	.105E-02	.241E-03	.9884
.479E-02	.960E-02	.400E-03	.253E-03	.946E-03	.228E-03	.9886
.437E-02	.961E-02	.390E-03	.247E-03	.850E-03	.216E-03	.9887
.398E-02	.962E-02	.380E-03	.240E-03	.764E-03	.205E-03	.9888
.363E-02	.963E-02	.370E-03	.234E-03	.686E-03	.194E-03	.9889
.331E-02	.964E-02	.360E-03	.227E-03	.615E-03	.184E-03	.9890
.302E-02	.965E-02	.351E-03	.221E-03	.551E-03	.174E-03	.9891
.275E-02	.966E-02	.342E-03	.215E-03	.493E-03	.165E-03	.9891
.251E-02	.967E-02	.333E-03	.209E-03	.441E-03	.156E-03	.9892
.229E-02	.968E-02	.324E-03	.204E-03	.394E-03	.147E-03	.9893
.209E-02	.969E-02	.315E-03	.198E-03	.351E-03	.139E-03	.9893
.191E-02	.969E-02	.306E-03	.192E-03	.313E-03	.131E-03	.9894
.174E-02	.970E-02	.297E-03	.187E-03	.278E-03	.124E-03	.9894
.158E-02	.971E-02	.289E-03	.181E-03	.247E-03	.117E-03	.9895
.145E-02	.972E-02	.281E-03	.176E-03	.219E-03	.110E-03	.9895
.132E-02	.973E-02	.272E-03	.170E-03	.194E-03	.103E-03	.9895
.120E-02	.974E-02	.264E-03	.165E-03	.171E-03	.971E-04	.9896
.110E-02	.974E-02	.256E-03	.160E-03	.151E-03	.912E-04	.9896

(a)

TS	HCLO	INCL1	HCL1	HCL2	TD	
850.	.100E-01	.989E-02	.105E-03	.100E-03	700.	
PH30	INCL	HCL	PH3	P4	P2	H2
.100E+00	.925E-02	.854E-03	.555E-03	.241E-01	.115E-02	.9641
.912E-01	.926E-02	.837E-03	.543E-03	.220E-01	.110E-02	.9663
.832E-01	.928E-02	.820E-03	.530E-03	.200E-01	.105E-02	.9683
.759E-01	.930E-02	.803E-03	.518E-03	.182E-01	.100E-02	.9702
.692E-01	.931E-02	.786E-03	.505E-03	.165E-01	.955E-03	.9719
.631E-01	.933E-02	.770E-03	.497E-03	.151E-01	.911E-03	.9734
.575E-01	.935E-02	.754E-03	.488E-03	.137E-01	.869E-03	.9749
.525E-01	.936E-02	.738E-03	.477E-03	.125E-01	.829E-03	.9761
.479E-01	.938E-02	.722E-03	.464E-03	.113E-01	.790E-03	.9773
.437E-01	.939E-02	.707E-03	.454E-03	.103E-01	.753E-03	.9784
.398E-01	.941E-02	.691E-03	.446E-03	.936E-02	.718E-03	.9794
.363E-01	.942E-02	.677E-03	.436E-03	.851E-02	.685E-03	.9803
.331E-01	.944E-02	.662E-03	.423E-03	.773E-02	.653E-03	.9811
.302E-01	.945E-02	.647E-03	.415E-03	.702E-02	.622E-03	.9818
.275E-01	.947E-02	.633E-03	.405E-03	.638E-02	.593E-03	.9825
.251E-01	.948E-02	.619E-03	.395E-03	.577E-02	.565E-03	.9831
.229E-01	.949E-02	.606E-03	.388E-03	.526E-02	.539E-03	.9837
.209E-01	.951E-02	.592E-03	.378E-03	.478E-02	.513E-03	.9842
.191E-01	.952E-02	.579E-03	.368E-03	.433E-02	.489E-03	.9847
.174E-01	.953E-02	.566E-03	.360E-03	.393E-02	.466E-03	.9851
.158E-01	.955E-02	.553E-03	.352E-03	.357E-02	.443E-03	.9855
.145E-01	.956E-02	.540E-03	.343E-03	.323E-02	.422E-03	.9859
.132E-01	.957E-02	.528E-03	.336E-03	.293E-02	.402E-03	.9862
.120E-01	.958E-02	.516E-03	.327E-03	.265E-02	.383E-03	.9865
.110E-01	.960E-02	.504E-03	.319E-03	.240E-02	.364E-03	.9868
.100E-01	.961E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9871
.912E-02	.962E-02	.481E-03	.304E-03	.197E-02	.330E-03	.9873
.832E-02	.963E-02	.470E-03	.296E-03	.178E-02	.313E-03	.9875
.759E-02	.964E-02	.458E-03	.289E-03	.161E-02	.298E-03	.9877
.692E-02	.965E-02	.448E-03	.282E-03	.146E-02	.283E-03	.9879
.631E-02	.966E-02	.437E-03	.275E-03	.132E-02	.269E-03	.9880
.575E-02	.967E-02	.426E-03	.268E-03	.119E-02	.256E-03	.9882
.525E-02	.968E-02	.416E-03	.261E-03	.107E-02	.243E-03	.9883
.479E-02	.969E-02	.406E-03	.254E-03	.967E-03	.231E-03	.9884
.437E-02	.970E-02	.396E-03	.248E-03	.872E-03	.219E-03	.9886
.398E-02	.971E-02	.386E-03	.242E-03	.786E-03	.208E-03	.9887
.363E-02	.972E-02	.376E-03	.235E-03	.707E-03	.197E-03	.9888
.331E-02	.973E-02	.367E-03	.229E-03	.636E-03	.187E-03	.9888
.302E-02	.974E-02	.358E-03	.223E-03	.572E-03	.178E-03	.9889
.275E-02	.975E-02	.349E-03	.217E-03	.514E-03	.168E-03	.9890
.251E-02	.976E-02	.340E-03	.212E-03	.462E-03	.160E-03	.9891
.229E-02	.977E-02	.331E-03	.206E-03	.414E-03	.151E-03	.9891
.209E-02	.978E-02	.322E-03	.201E-03	.371E-03	.143E-03	.9892
.191E-02	.979E-02	.314E-03	.195E-03	.333E-03	.135E-03	.9892
.174E-02	.979E-02	.305E-03	.190E-03	.298E-03	.128E-03	.9893
.158E-02	.980E-02	.297E-03	.185E-03	.266E-03	.121E-03	.9893
.145E-02	.981E-02	.289E-03	.180E-03	.238E-03	.115E-03	.9894
.132E-02	.982E-02	.282E-03	.174E-03	.213E-03	.108E-03	.9894
.120E-02	.983E-02	.274E-03	.170E-03	.190E-03	.102E-03	.9894
.110E-02	.983E-02	.266E-03	.165E-03	.169E-03	.966E-04	.9895

(b)

Table 9. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of the indium deposited, f_{In}, for different input PH_3 partial pressures, PH30, when the downstream HCl concentrations are 0 and 10^{-4} atm.

TS	TD	HCL2	HCL0	HCL2	
850.	700.	0.0000	.01	.0001	
PH30	INCL1	INCL	f_{In}	INCL	f_{In}
.100E+00	.9895E-02	.9154E-02	.0748	.9246E-02	.0656
.912E-01	.9895E-02	.9172E-02	.0731	.9263E-02	.0638
.832E-01	.9895E-02	.9189E-02	.0714	.9280E-02	.0621
.759E-01	.9895E-02	.9205E-02	.0697	.9297E-02	.0604
.692E-01	.9895E-02	.9222E-02	.0680	.9314E-02	.0587
.631E-01	.9895E-02	.9238E-02	.0664	.9330E-02	.0570
.575E-01	.9895E-02	.9254E-02	.0647	.9346E-02	.0554
.525E-01	.9895E-02	.9270E-02	.0631	.9362E-02	.0538
.479E-01	.9895E-02	.9285E-02	.0616	.9378E-02	.0522
.437E-01	.9895E-02	.9301E-02	.0600	.9393E-02	.0507
.398E-01	.9895E-02	.9316E-02	.0585	.9409E-02	.0491
.363E-01	.9895E-02	.9331E-02	.0570	.9423E-02	.0476
.331E-01	.9895E-02	.9345E-02	.0555	.9438E-02	.0461
.302E-01	.9895E-02	.9359E-02	.0541	.9453E-02	.0447
.275E-01	.9895E-02	.9374E-02	.0527	.9467E-02	.0432
.251E-01	.9895E-02	.9387E-02	.0513	.9481E-02	.0418
.229E-01	.9895E-02	.9401E-02	.0499	.9494E-02	.0404
.209E-01	.9895E-02	.9414E-02	.0485	.9508E-02	.0391
.191E-01	.9895E-02	.9428E-02	.0472	.9521E-02	.0377
.174E-01	.9895E-02	.9441E-02	.0459	.9534E-02	.0364
.158E-01	.9895E-02	.9453E-02	.0446	.9547E-02	.0351
.145E-01	.9895E-02	.9466E-02	.0433	.9560E-02	.0339
.132E-01	.9895E-02	.9478E-02	.0421	.9572E-02	.0326
.120E-01	.9895E-02	.9490E-02	.0409	.9584E-02	.0314
.110E-01	.9895E-02	.9502E-02	.0397	.9596E-02	.0302
.100E-01	.9895E-02	.9514E-02	.0385	.9608E-02	.0290
.912E-02	.9895E-02	.9525E-02	.0373	.9619E-02	.0278
.832E-02	.9895E-02	.9537E-02	.0362	.9630E-02	.0267
.759E-02	.9895E-02	.9548E-02	.0351	.9642E-02	.0256
.692E-02	.9895E-02	.9559E-02	.0340	.9652E-02	.0245
.631E-02	.9895E-02	.9569E-02	.0329	.9663E-02	.0234
.575E-02	.9895E-02	.9580E-02	.0318	.9674E-02	.0223
.525E-02	.9895E-02	.9590E-02	.0308	.9684E-02	.0213
.479E-02	.9895E-02	.9600E-02	.0297	.9694E-02	.0202
.437E-02	.9895E-02	.9610E-02	.0287	.9704E-02	.0192
.398E-02	.9895E-02	.9620E-02	.0277	.9714E-02	.0183
.363E-02	.9895E-02	.9630E-02	.0267	.9724E-02	.0173
.331E-02	.9895E-02	.9640E-02	.0258	.9733E-02	.0163
.302E-02	.9895E-02	.9649E-02	.0248	.9742E-02	.0154
.275E-02	.9895E-02	.9658E-02	.0239	.9751E-02	.0145
.251E-02	.9895E-02	.9667E-02	.0230	.9760E-02	.0136
.229E-02	.9895E-02	.9676E-02	.0220	.9769E-02	.0127
.209E-02	.9895E-02	.9685E-02	.0212	.9778E-02	.0118
.191E-02	.9895E-02	.9694E-02	.0203	.9786E-02	.0110
.174E-02	.9895E-02	.9703E-02	.0194	.9795E-02	.0101
.158E-02	.9895E-02	.9711E-02	.0185	.9803E-02	.0093
.145E-02	.9895E-02	.9719E-02	.0177	.9811E-02	.0085
.132E-02	.9895E-02	.9728E-02	.0169	.9818E-02	.0077
.120E-02	.9895E-02	.9736E-02	.0161	.9826E-02	.0069
.110E-02	.9895E-02	.9744E-02	.0153	.9834E-02	.0062

reason P_{HCl}, but it appears to be larger because the plot is a log-log plot. The partial pressures of the phosphorous containing compounds increase because the PH_3^o pressure increases faster than the InP deposition. P_{P_4} increases more rapidly than P_{P_2} and P_{PH_3} due to the fact that in this temperature-pressure region the enthalpy has a stronger effect than the entropy.

Again in Table 8b it is seen that introducing HCl downstream reduces the deposition reaction, since for a given PH_3^o concentration P_{InCl} is greater when HCl^2 has been introduced.

That increasing $P_{PH_3^o}$ increases the deposition of InP and introducing HCl^2 reduces it, is shown in Figure 14 and Table 9 where the dependence of f_{In} on $P_{PH_3^o}$ is illustrated.

F. The Effects of Varying HCl^2

In the previous sections it was shown that introducing HCl downstream reduces the tendency for InP to deposit. In this section this tendency is discussed in more detail. In Figure 15 and Table 10 it is seen that all of the constituent partial pressures increase slightly with P_{HCl^2} up to $P_{HCl^2} = 4 \times 10^{-4}$ atm. at which point deposition ceases. The HCl concentration increases because P_{HCl^2} increases faster than the rate of deposition of InP decreases, and the other pressures increase since there is less InP deposited.

That increasing the HCl^2 concentration reduces the deposition of InP is also shown in Figure 16 and Table 11 where f_{In} is determined as a function of P_{HCl^2}. The value of f_{In} decreases with increasing P_{HCl^2}, and the rate of decrease increases as P_{HCl^2} approaches the value of P_{HCl}.

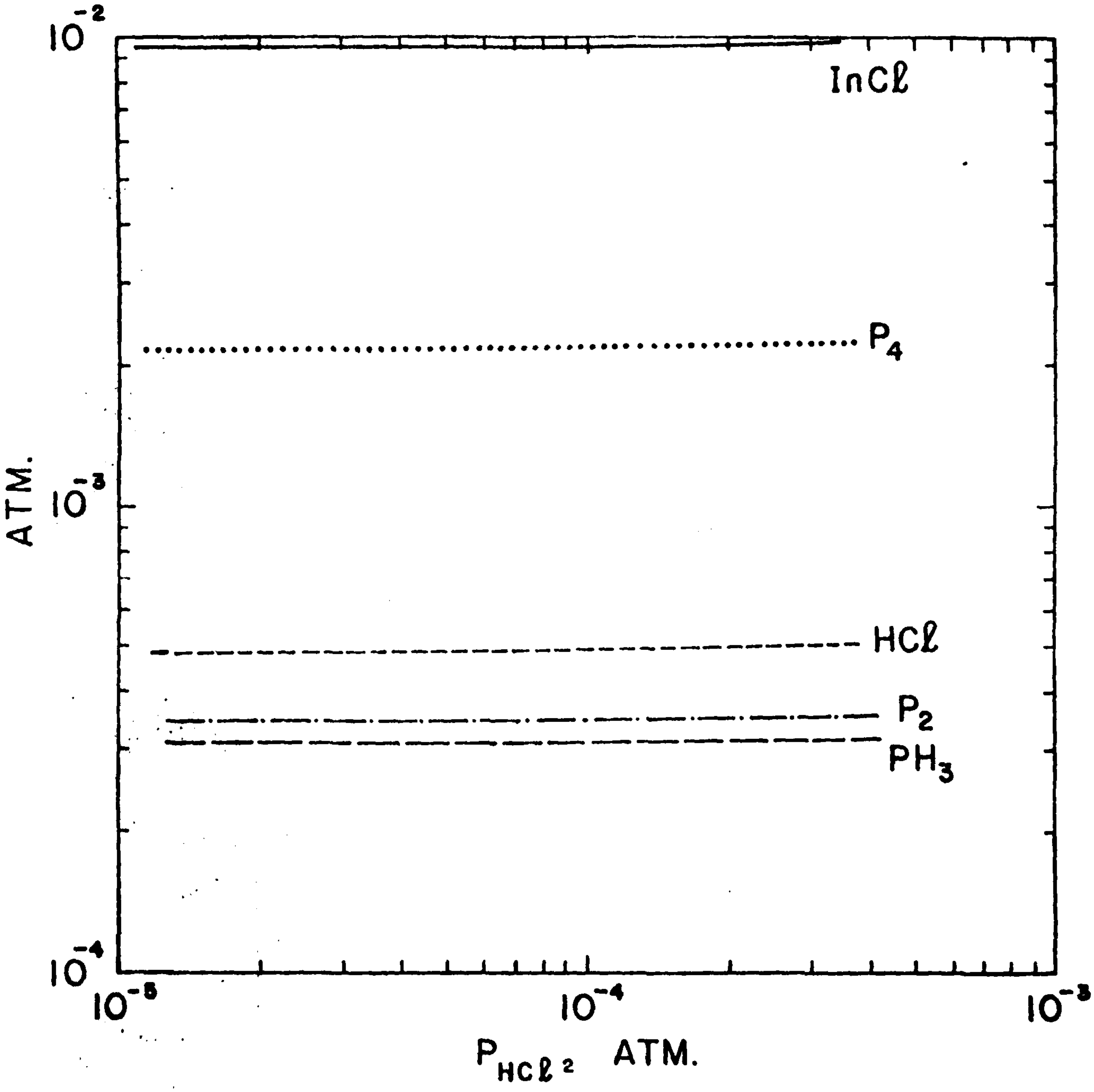


Fig. 15. The InCl, HCl, PH_3, P_4, and P_2 equilibrium partial pressures plotted as a function of the downstream input HCl concentration, HCl^2, when T_S = 850°C, T_D = 700°C, HCl^o = .01 atm., and PH_3^o = .01 atm.

Table 10. The equilibrium InCl, HCl, PH_3, P_4, P_2 and H_2 partial pressures calculated for different input downstream HCl concentrations, HCl^2, when T_S = 850°C, T_D = 700°C, HCl^o = .01 atm., and PH_3^o = .01 atm.

TS	PO	INCL1	HCL1	TD	PH30	P2IN
850.	.100E-01	.967E-02	.105E-03	700.	.100E-01	1.0007
HCL2	INCL	HCL	PH3	P4	P2	H2
.110E-04	.952E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.120E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.132E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.145E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.158E-04	.953E-02	.487E-03	.310E-03	.216E-02	.345E-03	.9872
.174E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.191E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.209E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.229E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.251E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.275E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.302E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.331E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9871
.363E-04	.955E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9871
.398E-04	.955E-02	.489E-03	.311E-03	.216E-02	.345E-03	.9871
.437E-04	.955E-02	.489E-03	.311E-03	.216E-02	.345E-03	.9871
.479E-04	.956E-02	.489E-03	.311E-03	.217E-02	.345E-03	.9871
.525E-04	.956E-02	.489E-03	.311E-03	.217E-02	.346E-03	.9871
.575E-04	.957E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9871
.631E-04	.957E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9871
.692E-04	.958E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9871
.759E-04	.959E-02	.491E-03	.311E-03	.217E-02	.346E-03	.9871
.832E-04	.959E-02	.491E-03	.311E-03	.217E-02	.346E-03	.9871
.912E-04	.960E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9871
.100E-03	.961E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9871
.110E-03	.962E-02	.493E-03	.311E-03	.218E-02	.347E-03	.9871
.120E-03	.963E-02	.494E-03	.312E-03	.218E-02	.347E-03	.9870
.132E-03	.964E-02	.494E-03	.312E-03	.218E-02	.347E-03	.9870
.145E-03	.965E-02	.495E-03	.312E-03	.219E-02	.347E-03	.9870
.158E-[illegible]	.966E-02	.496E-03	.312E-03	.219E-02	.347E-03	.9870
.174E-03	.968E-02	.497E-03	.312E-03	.219E-02	.348E-03	.9870
.191E-03	.969E-02	.498E-03	.312E-03	.220E-02	.348E-03	.9870
.209E-03	.971E-02	.499E-03	.312E-03	.220E-02	.348E-03	.9869
.229E-03	.973E-02	.500E-03	.312E-03	.221E-02	.349E-03	.9869
.251E-03	.975E-02	.501E-03	.313E-03	.221E-02	.349E-03	.9869
.275E-03	.977E-02	.503E-03	.313E-03	.222E-02	.350E-03	.9868
.302E-03	.980E-02	.505E-03	.313E-03	.222E-02	.350E-03	.9868
.331E-03	.982E-02	.506E-03	.313E-03	.223E-02	.351E-03	.9868
.363E-03	.985E-02	.508E-03	.313E-03	.224E-02	.351E-03	.9867
.398E-03	.989E-02	.510E-03	.314E-03	.224E-02	.352E-03	.9867

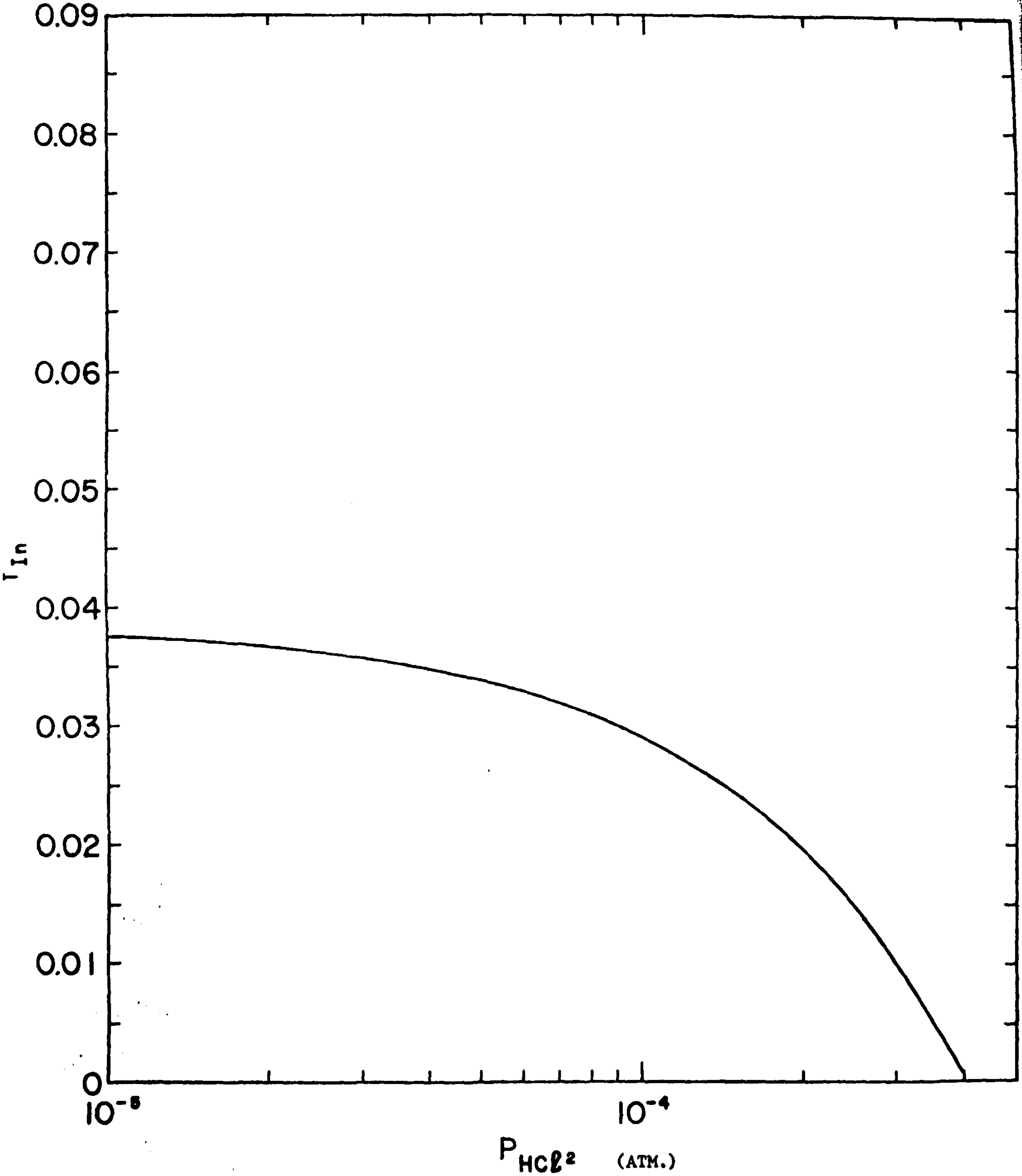


Fig. 16. The fraction of indium deposited, f_{In}, plotted as a function of the downstream HCl partial pressure, $P_{HCl}2$.

Table 11. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited, f_{In}, for different downstream HCl concentrations, HCL2.

TS	TD	FH50	HCLO
850.	700.	.01	.01
HCL2	INCL1	INCL	f_{In}
.100E-04	.9895E-02	.9523E-02	.0375
.110E-04	.9895E-02	.9524E-02	.0374
.120E-04	.9895E-02	.9525E-02	.0373
.132E-04	.9895E-02	.9526E-02	.0372
.145E-04	.9895E-02	.9527E-02	.0371
.158E-04	.9895E-02	.9529E-02	.0370
.174E-04	.9895E-02	.9530E-02	.0368
.191E-04	.9895E-02	.9532E-02	.0367
.209E-04	.9895E-02	.9533E-02	.0365
.229E-04	.9895E-02	.9535E-02	.0363
.251E-04	.9895E-02	.9537E-02	.0361
.275E-04	.9895E-02	.9540E-02	.0359
.302E-04	.9895E-02	.9542E-02	.0356
.331E-04	.9895E-02	.9545E-02	.0353
.363E-04	.9895E-02	.9548E-02	.0350
.398E-04	.9895E-02	.9551E-02	.0347
.437E-04	.9895E-02	.9555E-02	.0343
.479E-04	.9895E-02	.9559E-02	.0339
.525E-04	.9895E-02	.9563E-02	.0335
.575E-04	.9895E-02	.9568E-02	.0330
.631E-04	.9895E-02	.9573E-02	.0325
.692E-04	.9895E-02	.9579E-02	.0319
.759E-04	.9895E-02	.9585E-02	.0313
.832E-04	.9895E-02	.9592E-02	.0306
.912E-04	.9895E-02	.9599E-02	.0298
.100E-03	.9895E-02	.9608E-02	.0290
.110E-03	.9895E-02	.9617E-02	.0281
.120E-03	.9895E-02	.9627E-02	.0271
.132E-03	.9895E-02	.9638E-02	.0260
.145E-03	.9895E-02	.9650E-02	.0248
.158E-03	.9895E-02	.9663E-02	.0234
.174E-03	.9895E-02	.9677E-02	.0220
.191E-03	.9895E-02	.9693E-02	.0204
.209E-03	.9895E-02	.9710E-02	.0187
.229E-03	.9895E-02	.9729E-02	.0167
.251E-03	.9895E-02	.9750E-02	.0146
.275E-03	.9895E-02	.9773E-02	.0123
.302E-03	.9895E-02	.9797E-02	.0098
.331E-03	.9895E-02	.9825E-02	.0070
.363E-03	.9895E-02	.9855E-02	.0040
.398E-03	.9895E-02	.9888E-02	.0007

G. Silicon Contamination

It is thought that one of the primary contaminants in systems grown in silica growth tubes is silicon, and that the silicon activity increases as the HCl concentration decreases.[17,18] This is a consequence of the fact that the HCl discourages the decomposition of the chlorosilanes more than it encourages their formation from reactions with the SiO_2 growth tube. In the previous sections it was shown that the best way to increase the HCl concentration is to increase the source input HCl concentration, HCl^o. Thus, computations were made of the silicon activity as a function of P_{HCl^o} at three different temperatures.

Following the formalim of Dilorenzo[18] and Chaudhury,[17] the activity of silicon is found by examining the formation and decomposition of the silicon chlorides. According to Lever[19] these should include the chlorosilanes and $SiCl_2$. The chlorosilanes are formed by the following reaction

$$SiO_2(s) + nHCl + (4-n)H_2 \rightarrow SiCl_nH_{4-n} + 2H_2O \tag{29}$$

and the reaction for the formation of $SiCl_2$ is

$$SiO_2(s) + 2HCl + H_2 \rightarrow SiCl_2 + 2H_2O \quad . \tag{30}$$

The sum of the silicon chloride partial pressures is

$$P_{SiCl_2} + \sum P_{SiCl_nH_{4-n}} = (K_{SiCl_2} P^2_{HCl} P_{H_2} + \sum K_{SiCl_nH_{4-n}} P^n_{HCl} P^{4-n}_{H_2})/P^2_{H_2O} \tag{31}$$

For the decomposition reaction

$$SiCl_n H_{4-n} \rightarrow Si + nHCl + (2-n) H_2 \tag{32}$$

and

$$SiCl_2 \rightarrow Si + 2HCl - H_2 \tag{33}$$

the sum of the silicon chloride partial pressures is

$$P_{SiCl_2} + \sum P_{SiCl_nH_{4-n}} = \frac{a_{Si}\, P^2_{HCl}\, P^{-1}_{H_2}}{K'_{SiCl_2}} + a_{Si} \sum \frac{P^n_{HCl}\, P^{2-n}_{H_2}}{K'_{SiCl_nH_{4-n}}} \tag{34}$$

where the prime (') is used to differentiate the decomposition reaction from the formation reaction. From an oxygen balance it is seen that

$$P_{H_2O} = 2\,(P_{SiCl_2} + \sum P_{SiCl_nH_{4-n}})$$

$$= \{2[K_{SiCl_2}\, P^2_{HCl}\, P_{H_2} + \sum K_{SiCl_n}\, H_{4-n}\, P^n_{HCl}\, P^{4-n}_{H_2}]\} \tag{35}$$

so that

$$a_{Si} = P_{H_2O}/2\, \{\frac{P^2_{HCl}\, P^{-1}_{H_2}}{K'_{SiCl_2}} + \sum \frac{P^n_{HCl}\, P^{2-n}_{H_2}}{K'_{SiCl_n\, H_{4-n}}}\} \quad . \tag{36}$$

The equilibrium constants are determined using the free energy to absolute temperature ratios computed using the JANAF[20] tables, and they are listed in Table 12. The P_{HCl} and P_{H_2} values are those which are calculated in Section II-D.

The activity of silicon is plotted as a function of P_{HCl^o}. There it is seen that a(Si) decreases as the HCl concentration increases and the temperature decreases. It decreases with increasing temperature both because P_{HCl} increases with decreasing temperature and the equilibrium constants change in such a way that for a given HCl concentration, a(Si) decreases with decreasing temperature. The effects are large as a(Si)

can vary from a high of 3.9×10^{-3} cm^{-3} for T_D = 1100 K and P_{HCl^o} = .001 atm. to a low of 9.1×10^{-8} cm^{-3} for T_D = 900 K and P_{HCl^o} = .1 atm. (Note that these computations are for °K and not °C as were the previous computations since in this case the JANAF tables were used).

Table 12. The free energy to absolute temperature ratio for the formation and decomposition of the silicon chlorides.

	FORMATION					DECOMPOSITION				
	ΔG/T (cal./K)									
T° (K)	$SiClH_3$	$SiCl_2H_2$	$SiCl_3H$	$SiCl_4$	$SiCl_2$	$SiClH_3$	$SiCl_2H_2$	$SiCl_3H$	$SiCl_4$	$SiCl_2$
900	86.810	85.095	74.375	56.779	93.726	6.581	8.284	19.005	36.601	-.346
1000	78.962	77.656	68.442	53.241	82.268	3.530	4.826	14.040	29.241	.214
1100	72.582	71.601	63.605	50.358	72.929	1.035	2.007	10.002	23.250	.669

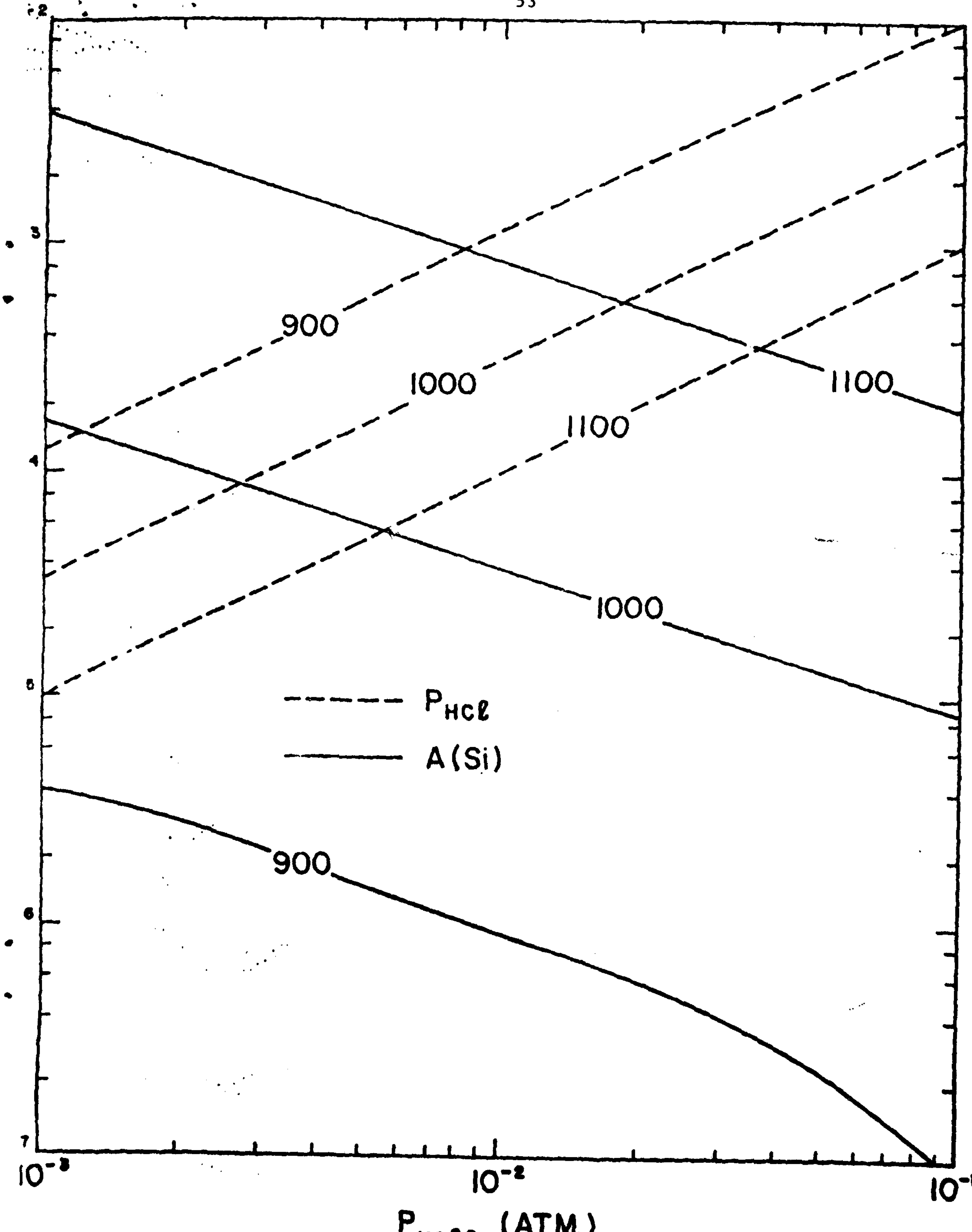


Fig. 17. The equilibrium HCl concentration (----) and the silicon activity, *a(Si)* (——), for T = 900, 1000 and 1100K plotted as a function of the source input HCl partial pressure, HCl^o.

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